METHOD AND COMPOSITION FOR USING STABILIZED BETA-CAROTENE AS CETANE IMPROVER IN HYDROCARBONACEOUS DIESEL FUELS

Field of the Invention

A diesel fuel additive is provided that includes beta-carotene stabilized with 2,2,4-trimethyl-6-ethoxy-1,2-dihydroquinoline. The additive may be added to any liquid hydrocarbon fuel, solid hydrocarbon fuel, or other hydrocarbonaceous combustible fuel to reduce emissions of undesired components during combustion of the fuel, provide improved fuel economy, engine cleanliness, and/or performance. A method for preparing the additive is also provided.

Background of the Invention

Hydrocarbon fuels typically contain a complex mixture of hydrocarbons, namely, molecules containing various configurations of hydrogen and carbon atoms. They may also contain various additives, including detergents, anti-oxidants, anti-icing agents, emulsifiers, corrosion inhibitors, dyes, deposit modifiers, and non-hydrocarbons such as oxygenates.

When such hydrocarbon fuels are combusted, a variety of pollutants are generated. These combustion products include ozone, particulates, carbon monoxide, nitrogen dioxide, sulfur dioxide, and lead. Both the U.S. Environmental Protection Agency (EPA) and the California Air Resources Board (CARB) have adopted ambient air quality standards directed to these pollutants. Both agencies have also adopted specifications for lower-emission gasolines.

The Phase II California Reformulated Gasoline (CaRFG2) regulations became operative in March 1, 1996. Governor Davis signed Executive Order D-5-99 on March 25, 1999, which directs the phase-out of methyl tertiary butyl ether (MTBE) in California's gasoline by December 31, 2002. The Phase III California Reformulated Gasoline (CaRFG3) regulations were approved on August 3, 2000, and became operative on September 2, 2000. The CaRFG2 and CaRFG3 standards are presented in Table A.

Table A
The California Reformulated Gasoline Phase 2 and Phase 3 Specifications

Property	Flat Limits			Averaging Limits			Cap Limits		
	CaRFG Phase I	CaRFG Phase II	CaRFG Phase III	CaRFG Phase I	CaRFG Phase II	CaRFG Phase III	CaRFG Phase I	CaRFG Phase II	CaRFG Phase III
Reid Vapor Pressure (psi)	n/a	7.0	7.0 or 6.9	7.8	n/a	n/a	n/a	7.0	6.4 - 7.2
Sulfur Content (wt. ppm)	n/a	40	20	151	30	15	n/a	80	60
									30

Property	Flat Limits			Averaging Limits			Cap Limits		
	CaRFG Phase I	CaRFG Phase II	CaRFG Phase III	CaRFG Phase I	CaRFG Phase II	CaRFG Phase III	CaRFG Phase I	CaRFG Phase II	CaRFG Phase III
Benzene Content (vol. %)	n/a	1.0	0.8	1.7	0.8	0.7	n/a	1.2	1.1
Aromatics Content (vol. %)	n/a	25	25	32	22	22	n/a	30	35
Olefins Content (vol. %)	n/a	6.0	6.0	9.6	4.0	4.0	n/a	10.0	10.0
T50 (°F)	n/a	210	213	212	200	203	n/a	220	220
T90 (°F)	n/a	300	305	329	290	295	n/a	330	330
Oxygen Content (wt. %)	n/a	1.8 - 2.2	1.8 - 2.2	n/a	n/a	n/a	n/a	1.8 - 3.5 / 0 - 3.5	1.8 - 3.5 / 0 - 3.5
MTBE and Other Oxygenates (other than ethanol)	n/a	n/a	Prohibited	n/a	n/a	n/a	n/a	n/a	Prohibited

n/a = not applicable

Considerable effort has been expended by the major oil companies to formulate gasolines that comply with the EPA and CARB standards. The most common approach to formulating compliant gasolines involves adjusting refinery processes so as to produce a gasoline base fuel meeting the specifications set forth above. Such an approach suffers a number of drawbacks, including the high costs involved in reconfiguring a refinery process, possible negative effects on the quantity or quality of other refinery products, and the inflexibility associated with having to produce a compliant base gasoline.

As with gasoline, diesel fuels may also be subject to regulation. Diesel fuels of poor quality may not be suitable for use until and unless they are brought up to specification. This is also typically accomplished in a refinery-based process, which suffers the same drawbacks as described above for refinery process for upgrading gasoline base fuel.

Summary of the Invention

Conventional refinery-based processes for producing quality diesel fuels of acceptable cetane number suffer from a number of drawbacks. A method of producing quality diesel fuels that does not suffer these drawbacks is therefore desirable. Methods of preparing beta-carotene-containing diesel fuel additives and diesel fuel, wherein the methods may be conducted under ambient conditions rather than an inert atmosphere as in prior art methods, is also desirable.

A diesel fuel additive is provided which may be combined with conventional diesel fuels so as to yield a diesel fuel with improved cetane number. Because an additive is used to produce improved diesel fuels, the equipment and product costs associated with a refinery solution are avoided. The additive may also be combined with other hydrocarbon fuels, such as gasoline fuels,

5   jet fuels, two-cycle fuels, coals, and other hydrocarbonaceous fuels to reduce the emission of pollutants during combustion of the fuel, to improve combustion, to improve fuel economy, and/or to provide other benefits.

In a first embodiment, a diesel fuel cetane improver is provided, the cetane improver including beta-carotene; and 2,2,4-trimethyl-6-ethoxy-1,2-dihydroquinoline.

10   In a second embodiment, a diesel fuel cetane improver is provided, the cetane improver including a cetane improving additive selected from the group consisting of carotenes, carotenoids, carotene derivatives, carotene precursors, carotenoid derivative, carotenoid precursors, long chain olefinic compounds, and mixtures thereof; and a stabilizing compound that inhibits oxidation of the cetane improving additive.

15   In an aspect of the second embodiment, the stabilizing compound includes 2,2,4-trimethyl-6-ethoxy-1,2-dihydroquinoline.

In an aspect of the second embodiment, the cetane improver further includes a plant oil extract and a thermal stabilizer.

In an aspect of the second embodiment, the plant oil extract includes an oil extract of a

20   plant of the *Leguminosae* family.

In an aspect of the second embodiment, the plant oil extract includes oil extract of barley.

In an aspect of the second embodiment, the plant oil extract includes chlorophyll.

In an aspect of the second embodiment, the thermal stabilizer includes jojoba oil.

In an aspect of the second embodiment, the thermal stabilizer includes an ester of a C20-

25   C22 straight chain monounsaturated carboxylic acid.

In an aspect of the second embodiment, the plant oil extract includes oil extract of barley and the thermal stabilizer includes jojoba oil.

In an aspect of the second embodiment, the cetane improver further includes a diluent.

In an aspect of the second embodiment, the diluent is selected from the group consisting of

30   toluene, gasoline, diesel fuel, jet fuel, and mixtures thereof.

In an aspect of the second embodiment, the cetane improver further includes an oxygenate.

In an aspect of the second embodiment, the oxygenate is selected from the group consisting of methanol, ethanol, methyl tertiary butyl ether, ethyl tertiary butyl ether, and tertiary amyl methyl ether, and mixtures thereof.

35   In an aspect of the second embodiment, the cetane improver further includes at least one additional additive selected from the group consisting of octane improvers, cetane improvers, detergents, demulsifiers, corrosion inhibitors, metal deactivators, ignition accelerators, dispersants,

anti-knock additives, anti-run-on additives, anti-pre-ignition additives, anti-misfire additives, antiwear additives, antioxidants, thermal stabilizers, plant oil extracts, demulsifiers, carrier fluids, solvents, fuel economy additives, emission reduction additives, lubricity improvers, and mixtures thereof.

5   In an aspect of the first embodiment, a ratio of grams of beta-carotene to grams of 2,2,4-trimethyl-6-ethoxy-1,2-dihydroquinoline in the additive is from about 20:1 to about 1:1.

           In an aspect of the first embodiment, a ratio of grams of beta-carotene to grams of 2,2,4-trimethyl-6-ethoxy-1,2-dihydroquinoline in the additive is from about 15:1 to about 5:1.

           In an aspect of the first embodiment, a ratio of grams of beta-carotene to grams of 2,2,4-
10   trimethyl-6-ethoxy-1,2-dihydroquinoline in the additive is about 10:1.

           In an aspect of the second embodiment, the diesel fuel cetane improver further includes 2-ethylhexyl nitrate.

           In a third embodiment, an additized diesel fuel is provided, the diesel fuel including a base fuel and a fuel additive for use in improving cetane number, the fuel additive including beta-
15   carotene; and 2,2,4-trimethyl-6-ethoxy-1,2-dihydroquinoline.

           In a fourth embodiment, an additized diesel fuel is provided, the diesel fuel including a base diesel fuel and a fuel additive for use in improving cetane number, the fuel additive including a cetane improving additive selected from the group consisting of carotenes, carotenoids, carotene derivatives, carotene precursors, carotenoid derivative, carotenoid precursors, long chain olefinic
20   compounds, and mixtures thereof; and a stabilizing compound that inhibits oxidation of the cetane improving additive.

           In an aspect of the fourth embodiment, the fuel includes from about 0.00025 g to about 0.05 g beta-carotene per 3785 ml additized diesel fuel and from about 0.000025 g to about 0.005 g ethoxyquin per 3785 ml additized diesel fuel.

25   In an aspect of the fourth embodiment, the fuel includes from about 0.00053 g to about 0.021 g beta-carotene per 3785 ml additized diesel fuel and from about 0.000053 g to about 0.0021 g ethoxyquin per 3785 ml additized diesel fuel.

           In a fifth embodiment, a method for producing an additized diesel fuel is provided, the method including the steps of preparing a first additive by combining beta-carotene, ethoxyquin,
30   jojoba oil, and a diluent, the first additive including about 4 ml jojoba oil, about 4 g beta-carotene, and about 0.4 g ethoxyquin per 3785 ml of the first additive; preparing a second additive by combining an oil extract of barley, jojoba oil, and a diluent, the second additive including about 4 ml jojoba oil and about 19.36 g oil extract of barley per 3785 ml of the second additive; and adding the first additive and the second additive to a base diesel fuel to produce an additized diesel fuel,
35   such that the additized diesel fuel includes from about 0.15 ml to about 20 ml of the first additive per 3785 ml of additized diesel fuel and from about 0.3 ml to about 3.6 ml of the second additive per 3785 ml of additized diesel fuel.

In a fifth embodiment, a method for producing an additized diesel fuel is provided, the method including the steps of preparing a first additive by combining beta-carotene, ethoxyquin, jojoba oil, and a diluent, the first additive including about 32 ml jojoba oil, about 3.2 g ethoxyquin, about 32 g beta-carotene per 3785 ml of the first additive; preparing a second additive by
5   combining an oil extract of barley, jojoba oil, and a diluent, the second additive including about 32 ml jojoba oil and about 155 g oil extract of barley per 3785 ml of the second additive; and adding the first additive and the second additive to a base diesel fuel to produce an additized diesel fuel, such that the additized diesel fuel includes from about 0.0625 ml to about 0.625 ml of the first additive per 3785 ml of additized diesel fuel and from about 0.3 ml to about 0.45 ml of the second
10   additive per 3785 ml of additized diesel fuel.

In a sixth embodiment, a gum inhibitor for gasoline is provided, the gum inhibitor including 2,2,4-trimethyl-6-ethoxy-1,2-dihydroquinoline.

In a seventh embodiment, a gasoline composition including 2,2,4-trimethyl-6-ethoxy-1,2-dihydroquinoline is provided.
15   In an aspect of the seventh embodiment, the 2,2,4-trimethyl-6-ethoxy-1,2-dihydroquinoline is present in the gasoline composition at a concentration of about 50 to 1000 ppm.

In an aspect of the seventh embodiment, the 2,2,4-trimethyl-6-ethoxy-1,2-dihydroquinoline is present in the gasoline composition at a concentration of about 100 to 500 ppm.

In an aspect of the seventh embodiment, the 2,2,4-trimethyl-6-ethoxy-1,2-dihydroquinoline
20   is present in the gasoline composition at a concentration of about 200 to 400 ppm.

Detailed Description of the Preferred Embodiment

Introduction

The following description and examples illustrate preferred embodiments of the present invention in detail. Those of skill in the art will recognize that there are numerous variations and
25   modifications of this invention that are encompassed by its scope. Accordingly, the description of preferred embodiments should not be deemed to limit the scope of the present invention.

Cetane Improving Additive Formulation

The emissions reduction additive formulation contains two components: beta-carotene or a suitable substitute, as described below, and 2,2,4-trimethyl-6-ethoxy-1,2-dihydroquinoline or a
30   suitable substitute, as described below. In preferred embodiments, the additive formulation further contains as an optional additive a conventional cetane-improving additive, such as 2-ethylhexyl nitrate.

Virtually all practical uses of fossil energy involve combustion processes, whereby a fuel is combined with oxygen from the air to release heat from oxidation reactions. The fuel and oxygen
35   will react when heated to a sufficiently high temperature, allowing a certain threshold energy level to be overcome. This threshold level, called the "Arrhenius Activation Energy," is strongly

dependent on temperature, with higher temperatures resulting in lower required energy levels. The activation energy can also be lowered by other factors, such as the presence of catalysts.

The additives of preferred embodiments may be different from catalysts, in that it is believed that they lower the activation energy and are consumed in the combustion process. In contrast, catalysts promote the reaction and lower the activation energy but are not consumed in the combustion process. While not wishing to be bound to any particular theory, it is believed that the active materials in the formulations of preferred embodiments, which are typically derived from plants and other renewable resource biodegradable materials, weaken the bonds of longer hydrocarbon chains at pre-combustion temperatures. The additives also bind oxygen from the fuel-air mixture, thus promoting the proximity of oxygen and hydrocarbons at a sub-molecular level. The improved mixing and lower activation energy may result in a more complete combustion process, reducing unwanted byproducts such as carbon monoxide and hydrocarbon emissions, while at the same time improving the overall efficiency of combustion. Lower combustion temperatures across a more even flame front also generally result in lower NOx emissions. Since the early work on tetraethyl lead and other antiknock agents by Charles F. Kettering and others in the 1920's, it has been recognized that small amounts of additives may have a substantial impact on the way a flame front propagates (or burns) within the cylinder of an internal combustion engine.

Although it is believed that certain components present in the formulations of preferred embodiments may bind oxygen for release during the combustion reaction process, they are not generally considered "oxygenates" as the term is conventionally used in the field of hydrocarbon-based fuel formulations. Oxygenates, such as methyl tert-butyl ether (MTBE) and ethanol are chemical compounds that contain oxygen in the molecular chain. When fuel and air are heated in the presence of an oxygenate, such as MTBE, the oxygenate decomposes at the onset of ignition, releasing free radicals. Free radicals facilitate the break-up of hydrocarbon chains, promoting combustion. Because oxygenates release their free radicals only once the ignition temperature is reached and because they suppress reactions ahead of the flame front, they also generally act as octane enhancers. When fuel and air are heated in the presence of the formulations of preferred embodiments, the components of the formulation contribute to weakening the hydrocarbon structure and capture oxygen. Proximity effects of the combustion agents lower the activation energy, accelerating combustion. The formulations of preferred embodiments may smooth out the flame front, providing a more uniform heat distribution, better stoichiometric (air to fuel ratio) combustion, and create a detergency effect that helps to prevent the build up of carbon deposits. The action of oxygenates can be compared to "pushing" oxygen into the combustion reaction by releasing it from their inherent molecular structures, whereas the formulations of preferred embodiments may be viewed as "pulling" oxygen out of the fuel-air mixture and into the combustion process.

While not wishing to be bound to any particular theory, it is believed that compounds containing a long hydrocarbon chain, (namely, a hydrocarbon chain comprising about five, six or seven carbon atoms, preferably about eight or nine carbon atoms, more preferably about 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20 or more carbon atoms) with one, two, three or more olefinic linkages

5   are particularly reactive under combustion conditions. Accordingly, long chain olefinic (unsaturated) compounds, such as beta-carotene, may provide an enhanced cetane improving effect, especially when compared to conventional cetane improving additives such as 2-ethylhexyl nitrate (2EHN).

It is known that a beta-carotene-containing additive prepared under an inert atmosphere and

10   added to a diesel fuel under an inert atmosphere is an effective cetane-improving additive for diesel fuel. See co-pending PCT Publication No. WO01/79398 filed April 12, 2001; U.S. Application No. 10/084,838 filed on February 26, 2002; U.S. Application No. 10/084,602 filed on February 26, 2002; U.S. Application No. 10/084,603 filed on February 26, 2002; U.S. Application No. 10/084,237 filed on February 26, 2002; U.S. Application No. 10/084,835 filed on February 26,

15   2002; U.S. Application No. 10/084,601 filed on February 26, 2002; U.S. Application No. 10/084,836 filed on February 26, 2002; U.S. Application No. 10/084,579 filed on February 26, 2002; U.S. Application No. 10/084,243 filed on February 26, 2002; U.S. Application No. 10/084,833 filed on February 26, 2002; U.S. Application No. 10/084,236 filed on February 26, 2002; U.S. Application No. 10/084,831 filed on February 26, 2002; PCT Application No.

20   US02/06137 filed on February 26, 2002; and Canadian Application No. 2,373,327 filed on February 26, 2002.

In contrast, when beta-carotene is added to diesel fuel according to conventional preparation methods (e.g., under ambient atmosphere), the beta-carotene rapidly loses its effectiveness as a cetane improver. The stability of beta-carotene and other carotenes and

25   carotenoids have been the subject of a number of studies, particularly in regard to the stability of such compounds in foods and food products. See, e.g., "Stability of Beta-Carotene in Isolated Systems" in J. Food Technol. (1979), 14(6), 571-8; "Use of Beta-Carotene in Extrusion-Cooking" in Ind. Aliment. Agric. (1986), 103(6), 527-32; "Thermal Degradation of Beta-Carotene - Formation of Nonvolatile Compound by Thermal Degradation of Beta-Carotene: Protection by

30   Antioxidants" in Methods in Enzymology, Vol. 213, (1992), Acad. Press, Inc., 129-142; U.S. 4,504,499 entitled "Heat-Stabilized, Carotenoid-Colored Edible Oils"; "Beta-Lactoglobulin Protects Beta-Ionone-Related Compound from Degradation by Heating, Oxidation, and Irradiation" in Biosci. Biotech. Biochem. (1995), 59(12), 2295-2297; "Study of the Effect of Some Antioxidants on the Stability of Beta-Carotene in an Ointment Containing Extracts from *Flos arnicae* and *Herba*

35   *calendulae*" in Herba Pol. (1981), 27(1), 39-43; "Thermal Degradation of All-Trans-Beta-Carotene in the Presence of Phenylalanine" in J. Sci. Food Agric. (1994), 65(4), 373-9; "Kinetics of All-Trans-Beta-Carotene Degradation on Heating With and Without Phenylalanine" in J. Am. Oil

Chem. Soc. (1994), 71(8), 893-6; "Proposal of a Mechanism for the Inhibition of All-Trans-Beta-Carotene Autoxidation at Elevated Temperature by N-(2-phenylethyl)-3,4-Diphenylpyrrole" in Food Chem. (1995), 54(3), 251-3; "The Stability of Beta-Carotene Under Different Laboratory Conditions" in J. Nutr. Biochem. (1992), 3(3), 124-8; "Inhibition of Beta-Carotene Oxidation in an Aromatic Solvent" in Izv. Akad. Nauk SSR, Ser. Khim. (1972), (2), 312-16; "Kinetics and. Mechanism of Oxidation and Stabilization of Beta-Carotene" in Vitam. Vitam. Prep. (1973), 232-40; "Efficient Search for New Antioxidants as Stabilizers of Carotene in Dehydrated Feeds" in Fiziol.-Biokhim. Osn. Povysh. Prod. Sel'skokhoz. Zhivotn. (1971), 232-41; and "Tetrahydroquinone Derivatives as Feed Antioxidants" in Sin. Issled. Eff. Khim. Polim. Mater. (1970), (4), 283-8.

Encapsulation of beta-carotene and other carotenoid and the use of other preservation and protection methods for improving stability have also been investigated. *See, e.g.*, "Comparison of Spray Drying, Drum Drying and Freeze Drying for Beta-Carotene Encapsulation and Preservation" in J. Food Sci. (1997), 62(6), 1158-1162; "Preservation of Beta-Carotene from Carrots" in Crit. Rev. Food Sci. Nutr. (1998), 38(5), 381-396; "Influence of Maltodextrin Systems at an Equivalent 25DE on Encapsulated Beta-Carotene" in J. Food Process. Preserv. (1999), 23(1), 39-55; "Kinetic Studies of Degradation of Saffron Carotenoids Encapsulated in Amorpohous Polymer Matrices" in Food Chemistry (2000), 71(2), 199-206; "Stability of Spray-Dried Encapsulated Carrot Carotenes" in J. Food Sci. (1995), 60(5), 1048-53.

None of these references, however, discusses stabilizers or preservation methods for use with beta-carotene or other carotenes and carotenoids when used as cetane improvers, much less the efficacy of such methods in enabling beta-carotene-containing cetane improvers to retain their cetane improving properties when prepared or added to fuel in ambient conditions, or in fuels stored under ambient conditions. Unexpectedly, it has been discovered that beta-carotene or other carotenes and carotenoids, when combined with certain stabilizing components or subjected to certain preservation techniques, retains its effectiveness as a cetane improving additive when formulated into an additive package under ambient conditions or when present in additized fuel stored under ambient conditions.

Beta-Carotene

One component of the formulations of preferred embodiments is beta-carotene. The beta-carotene may be added to the base formulation as a separate component in a purified form, or may be present or naturally occurring in another component, such as, for example, a plant oil extract as described below. Beta-Carotene is a high molecular weight antioxidant. In plants, it functions as a scavenger of oxygen radicals and protects chlorophyll from oxidation.

The beta-carotene may be natural or synthetic. In a preferred form, the beta-carotene is in natural form and contains a mixture of naturally occurring isomers, i.e., a mixture of the *cis* and *trans* isomers. In another preferred form, the beta-carotene is synthetic, but contains a mixture of

isomers similar to that observed for natural beta-carotene. In other embodiments, in may be preferred that the beta-carotene include only *trans*-beta-carotene, only *cis*-beta-carotene, or a mixture of the *cis* and *trans* isomers in various ratios. Other isomers, enantiomers, stereoisomers, or substituted forms of beta-carotene may also be suitable for use.

5   In a preferred embodiment, the beta-carotene is provided in a form equivalent to vitamin A having a purity of 1.6 million units of vitamin A activity. Vitamin A of lesser or greater purity may also be suitable for use. It may be desirable to adjust the amount of beta-carotene utilized depending upon the activity. It is particularly preferred to adjust the amount to yield an equivalent activity to 1.6 million units of vitamin A activity. For example, if the purity is 800,000 units of

10   vitamin A activity, the amount used is doubled to yield the desired activity.

Precursors, derivatives, or substituted versions, of beta-carotene or other carotenes or carotenoids, for example, vitamin A, may be suitable for use in preferred embodiments. Alkoxylated derivatives, including methoxylated and ethoxylated derivatives of carotenes and carotenoids may also be suitable for use, as well as esters of carotenes and carotenoids. Suitable

15   substituted versions may include hydrocarbyl substituted versions, including straight and branched hydrocarbyl groups, alkyl, alkenyl, aryl, alkylaryl, arylalkyl, cycloalkyl, alkynyl groups, and any combination thereof. Heteroatom substituted versions, or versions with other substituents may also be suitable for use. All isomeric forms, including stereoisomers, geometric isomers, optical isomers, enantiomers, and the like, are also suitable for use.

20   While beta-carotene is preferred in many embodiments, in other embodiments it may be desirable to substitute another carotene or carotenoid, for example, alpha-carotene or carotenoids as described below, for beta-carotene. Alternatively, another component may supplement the beta-carotene, including, but not limited to, alpha-carotene, or additional carotenoids from algae xeaxabthin, crypotoxanthin, lycopene, lutein, broccoli concentrate, spinach concentrate, tomato

25   concentrate, kale concentrate, cabbage concentrate, brussels sprouts concentrate and phospholipids, green tea extract, milk thistle extract, curcumin extract, quercetin, bromelain, cranberry and cranberry powder extract, pineapple extract, pineapple leaves extract, rosemary extract, grapeseed extract, ginkgo biloba extract, polyphenols, flavonoids, ginger root extract, hawthorn berry extract, bilberry extract, butylated hydroxytoluene (BHT), oil extract of marigolds, any and all oil extracts

30   of carrots, fruits, vegetables, flowers, grasses, natural grains, leaves from trees, leaves from hedges, hay, any living plant or tree, and combinations or mixtures thereof.

Vegetable carotenoids of guaranteed potency are particularly preferred, including those containing lycopene, lutein, alpha-carotene, other carotenoids from carrots or algae, betatene, and natural carrot extract. The vegetable carotenoids are particularly preferred as substitutes for beta-

35   carotene or in combination with beta-carotene.

Any suitable isomeric form or mixture of isomeric forms of carotenes or carotenoids may be employed in preferred embodiments. Pure carotenes or carotenoids, or mixtures of two or more

carotenes and/or carotenoids may also be suitable for use in certain embodiments. Suitable substitutes for the carotenes and carotenoids described above include compounds containing a long hydrocarbon chain, (namely, a hydrocarbon chain comprising about five, six or seven carbon atoms, preferably about eight or nine carbon atoms, more preferably about 10, 11, 12, 13, 14, 15, 16, 17,

5   18, 19, 20 or more carbon atoms) with one, two, three, or more olefinic linkages. Such compounds may be also be present in combination with the carotenes and/or carotenoids.

The carotene, carotenoid, or precursor, derivative, or substituted version thereof may be natural, e.g., plant derived, or synthetic. It may also be produced by genetically engineered, altered, or modified organisms, e.g., algae, bacteria, microorganisms, or plants. It may be particularly

10   preferred to utilize a carotene or carotenoid or related compound obtained from a plant that has been genetically engineered to yield relatively high levels of the compound, relatively high levels of a preferred isomeric form, or a particularly preferred ratio or combination of carotenes or carotenoids or other components.

While not wishing to be limited to any particular mechanism, it is believed that the beta-

15   carotene in the formulations of preferred embodiments may scavenge oxygen radicals in the combustion process or may act as an oxygen solubilizer or oxygen getter for the available oxygen that is present in the air/fuel stream for combustion.

The beta-carotene is typically added in a liquid form to the diesel fuel formulation. In addition to adding beta-carotene in a liquid form to a fuel formulation, beta-carotene may also be

20   added in solid form, for example, in dehydrated form, or in the form of an encapsulated liquid or solid, as described in detail below. The preservation and storage of solutions or suspensions of beta-carotene or other plant-based materials may carry benefits, such as reduced weight and storage space, and increased stability and resistance to oxidation. Beta-Carotene in dehydrated form may be prepared by methods including freeze-drying, vacuum or air-drying, lyophilization, spray-drying, fluidized bed

25   drying, and other preservation and dehydration methods as are known in the art. Beta-Carotene in dehydrated form may be added to fuel in the dehydrated form, or may be added as a reconstituted liquid in an appropriate solvent.   In a preferred embodiment, a solid containing beta-carotene is added to the fuel to be additized. Suitable solid forms include, but are not limited to, tablets, granules, powders, encapsulated solids and/or encapsulated liquids, and the like. Additional components may

30   also be present in the solid form. Any suitable encapsulating material may be used, preferably a polymeric or other material that is soluble in the fuel to be additized. The encapsulating material dissolves in the fuel, releasing the encapsulated material. The tablet preferably dissolves in the fuel over an acceptable period of time. Dissolving aids may be included in the tablet, e.g., small granules or particles of active ingredient may be present in a matrix with high solubility in the fuel. A combination

35   of solid and liquid dosing methods may be utilized, and the solid may be added to the fuel at any preferred time, e.g., by the consumer directly to a vehicle's fuel tank, to bulk fuel in the refinery, and

the like. In certain embodiments, it may be preferred to utilize a combination of additive forms, e.g., liquid and solid, as will be appreciated by one skilled in the art.

2,2,4-Trimethyl-6-Ethoxy-1,2-Dihydroquinoline

The beta-carotene or other long chain olefinic compound in the formulations of preferred embodiments is present in combination with a stabilizing compound. The stabilizing compound enables the beta-carotene to retain its cetane improving properties despite the presence of ambient atmosphere during the preparation of the additive package, the additization of the diesel fuel, or the storage of the diesel fuel.

In a particularly preferred embodiment, the stabilizing compound contains a quinoline moiety, preferably 2,2,4-trimethyl-6-ethoxy-1,2-dihydroquinoline, commonly referred to as ethoxyquin. The compound is marketed under the trademark SANTOQUIN® by Solutia Inc. of St. Louis, Missouri, and is widely used as an antioxidant for animal feed and forage.
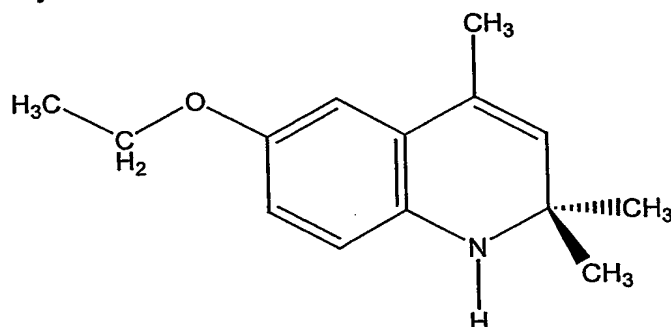
Other suitable stabilizing compounds for beta-carotene (or suitable substitutes such as carotenes, carotenoids, their derivatives and precursors, and long chain unsaturated compounds) include butylated hydroxyanisole; butylated hydroxytoluene; gallates such as octyl gallate, dodecyl gallate, and propyl gallate; fatty acid esters including, but not limited to, methyl esters such as methyl linoleate, methyl oleate, methyl stearate, and other esters such as ascorbic palmitate; disulfiram; tocopherols, such as gamma-tocopherol, delta-tocopherol and alpha-tocopherol, and tocopherol derivatives and precursors; deodorized extract of rosemary; propionate esters and thiopropionate esters such as lauryl thiodipropionate or dilauryl thiodipropionate; beta-lactoglobulin; ascorbic acid; amino acids such as phenylalanine, cysteine, tryptophan, methionine, glutamic acid, glutamine, arginine, leucine, tyrosine, lysine, serine, histidine, threonine, asparagine, glycine, aspartic acid, isoleucine, valine, and alanine; 2,2,6,6-tetramethylpiperidinooxy, also referred to as tanan; 2,2,6,6-tetramethyl-4-hydroxypiperidine-1-oxyl, also referred to as tanol; dimethyl-p-phenylaminophenoxysilane; di-p-anisylazoxides; 2,2,4-trimethyl-6-ethoxy-1,2,3,4-tetrahydroquinoline; dihydrosantoquin; santoquin; p-hydroxydiphenylamine, and carbonates, phthalates, and adipates thereof; and diludin, a 1,4-dihydropyridine derivative.

Particularly preferred stabilizing compounds for beta-carotene include oil-soluble antioxidants, including, but not limited to ascorbyl palmitate, butylated hydroxyanisole, butylated

hydroxytoluene, lecithin, propyl gallate, alpha-tocopherol, phenyl-alpha-naphthylamine, hydroquinone, nordihydroguaiaretic acid, rosemary extract, mixtures thereof, and the like.

Also preferred in certain embodiments as stabilizing compounds for beta-carotene are conventional synthetic and natural antioxidants. Synthetic and natural antioxidants include, but are not limited to, Vitamin C and derivatives (ascorbic acid); Vitamin E and derivatives (tocopherols & tocotrienols); flavonoids and derivatives (including catechins); phenolic acids and derivatives; tert-butyl hydroquinone (TBHQ); imidazolidinyl urea, quaternary ammoniums, diazolidinyl urea; erythorbic acid; sodium erythorbate, lactic acid, calcium ascorbate, sodium ascorbate, potassium ascorbate, ascorbyl stearate, erythorbin acid; sodium erythorbin; butylhydroxinon; sodium or potassium or calcium or magnesium lactate; citric acid; sodium, monosodium, disodium or trisodium citrates; potassium, monopotassium or tripotassium citrate; tartaric acid; sodium, monosodium or disodium tartrates; potassium, monopotassium tartrate or diipotassium tartrate; sodium potassium tartrate; phosphoric acid; sodium, monosodium, disodium or trisodium phosphates; potassium, monopotassium, dipotassium and tripotassium phosphates; stannous chloride; lecithin; nordihydroguaiaretic acid (NDGA); alcoholic esters of the gallates; ascorbyl stearate; 2-tertiarybutyl-4-hydroxyanisole; 3-tertiarybutyl-4-hydroxyanisole; l-cysteine hydrochloride; gum guaiacum; lecithin citrate; monoglyceride citrate; monoisopropyl citrate; Ethylenediaminetetraacetic acid; 2,6-di-tert-butyl-4-hydroxymethylphenol; polyphosphates; trihydroxy butyrophenone; and anoxomer.

Water soluble antioxidants such as ascorbic acid, sodium metabisulfite, sodium bisulfite, sodium thiosulfite, sodium formaldehyde sulfoxylate, isoascorbic acid, thioglyerol, thiosorbitol, thiourea, thioglycolic acid, cysteine hydrochloride, 1,4-diazobicyclo-(2,2,2)-octane, malic acid, fumaric acid, licopene and mixtures thereof, may also be suitable for use as stabilizing compounds for beta-carotene in preferred embodiments. Such water soluble components are preferably formulated into an emulsion compatible with diesel fuel, or encapsulated in a non-polar or oleophilic substance prior to addition to diesel fuel.

Other compounds that may be suitable for use as stabilizers include alkyl phenols, such as mono-butylphenols, tetrabutylphenols, tributylphenols, 2-tert-butylphenol, 2,6-di-tert-butylphenol, ethyl phenols, 2-tert-butyl-4-n-butylphenol, 2,4,6-tri-tert-butylphenol, and 2,6-di-tert-butyl-4-butylphenol; 2,6-di-t-butylphenol; 2,2'-methylene-bis(6-t-butyl-4-methylphenol); n-octadecyl 3-(3,5-di-t-butyl-4-hydroxyphenyl) propionate; 1,1,3-tris(3-t-butyl-6-methyl-4-hydroxyphenyl) butane; pentaerythrityl tetrakis[3-(3,5-di-t-butyl-4-hydroxyphenyl) propionate]; di-n-octadecyl(3,5-di-t-butyl-4-hydroxybenzyl) phosphonate; 2,4,6-tris(3,5-di-t-butyl-4-hydroxybenzyl) mesitylene; tris(3,5-di-t-butyl-4-hydroxybenzyl) isocyanurate; pentaerythritol co-esters derived from pentaerythritol, (3-alkyl-4-hydroxyphenyl)-alkanoic acids and alkylthioalkanoic acids or lower alkyl esters of such acids which are useful as stabilizers of organic material normally susceptible to oxidative and/or thermal deterioration; the reaction product of malonic acid, dodecyl aldehyde and

tallowamine; hindered phenyl phosphites; hindered piperidine carboxylic acids and metal salts thereof; acylated derivatives of 2,6-dihydroxy-9-azabicyclo[3.3.1]nonane; bicyclic hindered amines; sulfur containing derivatives of dialkyl-4-hydroxyphenyltriazine; bicyclic hindered amino acids and metal salts thereof; trialkylsubstituted hydroxybenzyl malonates; hindered piperidine
5   carboxylic acids and metal salts thereof; pyrrolidine dicarboxylic acids and ester; metal salts of N,N-disubstituted beta-alanines; hydrocarbyl thioalkylene phosphites; hydroxybenzyl thioalkylene phosphites; diphenylamines, dinaphthylamines, and phenylnaphthylamines, either substituted or unsubstituted, e.g., N,N'-diphenylphenylenediamine, p-octyldiphenylamine, p,p-dioctyldiphenylamine, N-phenyl-1-naphthylamine, N-phenyl-2-naphthylamine,
10   N-(p-dodecyl)phenyl-2-naphthylamine, di-1-naphthylamine, and di-2naphthylamine; phenothazines such as N-alkylphenothiazines; imino(bisbenzyl); emu oil; alpha-lipoic acid; and the like; and mixtures thereof.

      While not wishing to be bound to any particular mechanism or theory, it is believed that the stabilizing compound functions as a preservative or stabilizer by inhibiting oxidation of a carotene
15   or other long chain olefinic compound due to free radical formation. When the stabilizing compound is present in combination with beta-carotene, it is not necessary to prepare or store the fuel additive or the additized fuel under an inert atmosphere. This is in contrast to prior art methods wherein preparation and storage under an inert atmosphere were generally necessary in order to preserve the activity of the beta-carotene prior to combustion of the additized fuel. The
20   combination of a stabilizing compound such as ethoxyquin in combination with cetane improving compounds such as beta-carotene or long chain olefinic compounds may result in a synergistic increase in cetane number, as demonstrated in the examples below.

      Cetane Improvers

      In certain embodiments, the additive or diesel fuel may contain one or more conventional
25   cetane improvers and/or ignition accelerators. Preferred organic nitrates are substituted or unsubstituted alkyl or cycloalkyl nitrates having up to about 10 carbon atoms, preferably from 2 to 10 carbon atoms. The alkyl group may be either linear or branched. Specific examples of nitrate compounds suitable for use in preferred embodiments include, but are not limited to the following: methyl nitrate, ethyl nitrate, n-propyl nitrate, isopropyl nitrate, allyl nitrate, n-butyl nitrate, isobutyl
30   nitrate, sec-butyl nitrate, tert-butyl nitrate, n-amyl nitrate, isoamyl nitrate, 2-amyl nitrate, 3-amyl nitrate, tert-amyl nitrate, n-hexyl nitrate, 2-ethylhexyl nitrate, n-heptyl nitrate, sec-heptyl nitrate, n-octyl nitrate, sec-octyl nitrate, n-nonyl nitrate, n-decyl nitrate, n-dodecyl nitrate, cyclopentylnitrate, cyclohexylnitrate, methylcyclohexyl nitrate, isopropylcyclohexyl nitrate, and the esters of alkoxy substituted aliphatic alcohols, such as 1-methoxypropyl-2-nitrate, 1-ethoxpropyl-2 nitrate,
35   1-isopropoxy-butyl nitrate, 1-ethoxylbutyl nitrate and the like. Preferred alkyl nitrates are ethyl nitrate, propyl nitrate, amyl nitrates, and hexyl nitrates. Other preferred alkyl nitrates are mixtures of primary amyl nitrates or primary hexyl nitrates. By primary is meant that the nitrate functional

group is attached to a carbon atom which is attached to two hydrogen atoms. Examples of primary hexyl nitrates include n-hexyl nitrate, 2-ethylhexyl nitrate, 4-methyl-n-pentyl nitrate, and the like. Preparation of the nitrate esters may be accomplished by any of the commonly used methods: such as, for example, esterification of the appropriate alcohol, or reaction of a suitable alkyl halide with

5   silver nitrate. Another additive suitable for use in improving cetane and/or reducing particulate emissions is di-t-butyl peroxide.

Conventional ignition accelerators may also be used, such as hydrogen peroxide, benzoyl peroxide, di-tert-butyl peroxide, and the like. Moreover, certain inorganic and organic chlorides and bromides, such as, for example, aluminum chloride, ethyl chloride or bromide may find use in

10   the preferred embodiments as primers when used in combination with the other ignition accelerators.

Ratio of Beta-Carotene to Stabilizing Compound

In preferred embodiments, the components of the base additive formulation are present in specified ratios and are present in specific treat rates in the additized fuel. In determining the ratios

15   and treat rates of the components, factors taken into consideration may include elevation, base fuel purity, type of fuel (e.g., gasoline, diesel, residual fuel, two-cycle fuel, and the like), sulfur content, mercaptan content, olefin content, aromatic content and the engine or device using the fuel (e.g., gasoline powered engine, diesel engine, two-cycle engine, stationary boiler). For example, if a diesel fuel is of a lower grade, such as one that has a high sulfur content (1 wt. % or more), a high

20   olefin content (12 ppm or higher), or a high aromatics content (35 wt. % or higher), the ratios may be adjusted to compensate by providing additional beta-carotene.

In additive formulations and additized fuels of preferred embodiments, the ratio of grams of beta-carotene to grams ethoxyquin in the additive is generally from about 20:1 or greater to about 1:20 or lower; typically from about 19:1, 18:1, 17:1; 16:1, or 15:1 to about 1:15, 1:16, 1:17, 1:18; or

25   1:19; preferably from about 14:1, 13:1, 12:1, or 11:1 to about 1:11, 1:12; 1:13; or 1:14, more preferably from about 10:1, 9:1, 8:1, 7:1, 6:1, or 5:1 to about 1:5, 1:6, 1:7, 1:8, 1:9, or 1:10, and most preferably from about 4:1, 3:1, 2:1, or 1:1 to about 1:2, 1:3, or 1:4. These ratios are also generally preferred for the suitable substitutes of beta-carotene and suitable substitutes for ethoxyquin. However, if the stabilizer is less potent or effective than ethoxyquin, it may be

30   preferred to use proportionally more of the stabilizer in the additive combination. Likewise, if the stabilizer is more potent or effective than ethoxyquin, it may be preferred to use proportionally less of the stabilizer in the additive combination.

It is preferred that the ratio of beta-carotene and/or substitutes(s) to ethoxyquin and/or substitute(s) approach the above ratios. In certain embodiments, it may be preferred to adjust the

35   treat rate of ethoxyquin up or down, depending upon the oxidative severity of the fuel and the degree of stabilization to be provided the beta-carotene. The total treat rate of each component in the additized fuel may be adjusted up or down, depending upon various factors as described above.

Other Additives

The additive packages and formulated fuels compositions of preferred embodiments may contain additives other than the ones described above. These additives may include, but are not limited to, one or more octane improvers, detergents, antioxidants, demulsifiers, corrosion inhibitors and/or metal deactivators, diluents, cold flow improvers, thermal stabilizers, and the like, as described below.

Plant Oil Extracts

In a preferred embodiment, the formulation may include as an additional component a plant oil extracted from, e.g., vetch, hops, barley, or alfalfa. The term "plant oil extract" as used herein, is a broad term and is used in its ordinary sense, including, without limitation, those components present in the plant material which are soluble in n-hexane. Chlorophyll may be used as a substitute for, or in addition to, all or a portion of the oil extract. The hydrophobic oil extract contains chlorophyll. Chlorophyll is the green pigment in plants that accomplishes photosynthesis, the process in which carbon dioxide and water combine to form glucose and oxygen. The hydrophobic oil extract typically also contains many other compounds, including, but not limited to, organometallics, antioxidants, oils, lipids thermal stabilizers or the starting materials for these types of products, and approximately 300 other compounds primarily consisting of low to high molecular weight antioxidants.

While the oil extract from barley is preferred in many embodiments, in other embodiments it may be desirable to substitute, in whole or in part, another plant oil extract, including, but not limited to, alfalfa, hops oil extract, fescue oil extract, vetch oil extract, green clover oil extract, wheat oil extract, extract of the green portions of grains, green food materials oil extract, green hedges or green leaves or green grass oil extract, any flowers containing green portions, the leafy or green portion of a plant of any member of the legume family, chlorophyll or chlorophyll containing extracts, or combinations or mixtures thereof. Suitable legumes include legume selected from the group consisting of lima bean, kidney bean, pinto bean, red bean, soy bean, great northern bean, lentil, navy bean, black turtle bean, pea, garbanzo bean, and black eye pea. Suitable grains include fescue, clover, wheat, oats, barley, rye, sorghum, flax, tritcale, rice, corn, spelt, millet, amaranth, buckwheat, quinoa, kamut, and teff.

Especially preferred plant oil extracts are those derived from plants that are members of the *Fabaceae* (*Leguminosae*) plant family, commonly referred to as the pulse family, and also as the pea or legume family. The *Leguminosae* family includes over 700 genera and 17,000 species, including shrubs, trees, and herbs. The family is divided into three subfamilies: divided into three subfamilies: *Mimosoideae*, which are mainly tropical trees and shrubs; *Caesalpinioideae*, which include tropical and sub-tropical shrubs; and *Papilioniodeae* which includes peas and beans. A common feature of most members of the *Leguminosae* family is the presence of root nodules containing nitrogen-fixing *Rhizobium* bacteria. Many members of the *Leguminosae* family also

accumulate high levels of vegetable oils in their seeds. The *Leguminosae* family includes the lead-plant, hog peanut, wild bean, Canadian milk vetch, indigo, soybean, pale vetchling, marsh vetchling, veiny pea, round-headed bush clover, perennial lupine, hop clover, alfalfa, white sweet clover, yellow sweet clover, white prairie-clover, purple prairie-clover, common locust, small wild

5   bean, red clover, white clover, narrow-leaved vetch, hairy vetch, garden pea, chick pea, string green, kidney bean, mung bean, lima bean, broad bean, lentil, peanut or groundnut, and the cowpea, to name but a few.

The most preferred form of oil-extracted material consists of a material having a paste or mud-like consistency after extraction, namely, a solid or semi-solid, rather than a liquid, after

10   extraction. Such pastes typically contain a higher concentration of Chlorophyll A to Chlorophyll B in the extract. The color of such a material is generally a deep black-green with some degree of fluorescence throughout the material. Such a material can be recovered from many or all the plant sources enumerated for the *Leguminosae* family. While such a form is generally preferred for most embodiments, in certain other embodiments a liquid or some other form may be preferred.

15   The oil extract may be obtained using extraction methods well known to those of skill in the art. Solvent extraction methods are generally preferred. Any suitable extraction solvent may be used which is capable of separating the oil and oil-soluble fractions from the plant material. Nonpolar extraction solvents are generally preferred. The solvent may include a single solvent, or a mixture of two or more solvents. Suitable solvents include, but are not limited to, cyclic, straight

20   chain, and branched-chain alkanes containing from about 5 or fewer to 12 or more carbon atoms. Specific examples of acyclic alkane extractants include pentane, hexane, heptane, octane, nonane, decane, mixed hexanes, mixed heptanes, mixed octanes, isooctane, and the like. Examples of the cycloalkane extractants include cyclopentane, cyclohexane, cycloheptane, cyclooctane, methylcyclohexane, and the like. Alkenes such as hexenes, heptenes, octenes, nonenes, and

25   decenes are also suitable for use, as are aromatic hydrocarbons such as benzene, toluene, and xylene. Halogenated hydrocarbons such as chlorobenzene, dichlorobenzene, trichlorobenzene, methylene chloride, chloroform, carbon tetrachloride, perchloroethylene, trichloroethylene, trichloroethane, and trichlorotrifluoroethane may also be used. Generally preferred solvents are C6 to C12 alkanes, particularly n-hexane.

30   Hexane extraction is the most commonly used technique for extracting oil from seeds. It is a highly efficient extraction method that extracts virtually all oil-soluble fractions in the plant material. In a typical hexane extraction, the plant material is comminuted. Grasses and leafy plants may be chopped into small pieces. Seed are typically ground or flaked. The plant material is typically exposed to hexane at an elevated temperature. The hexane, a highly flammable, colorless,

35   volatile solvent that dissolves out the oil, typically leaves only a few weight percent of the oil in the residual plant material. The oil/solvent mixture may be heated to 212^{0} F, the temperature at which hexane flashes off, and is then distilled to remove all traces of hexane. Alternatively, hexane may

be removed by evaporation at reduced pressure. The resulting oil extract is suitable for use in the formulations of preferred embodiments.

Plant oils extracts for use in edible items or cosmetics typically undergo additional processing steps to remove impurities that may affect the appearance, shelf life, taste, and the like,
5   to yield a refined oil. These impurities may include phospholipids, mucilaginous gums, free fatty acids, color pigments and fine plant particles. Different methods are used to remove these by-products including water precipitation or precipitation with aqueous solutions of organic acids. Color compounds are typically removed by bleaching, wherein the oil is typically passed through an adsorbent such as diatomaceous clay. Deodorization may also be conducted, which typically
10   involves the use of steam distillation. Such additional processing steps are generally unnecessary. However, oils subjected to such treatments may be suitable for use in the formulations of preferred embodiments.

Other preferred extraction processes include, but are not limited to, supercritical fluid extraction, typically with carbon dioxide. Other gases, such as helium, argon, xenon, and nitrogen
15   may also be suitable for use as solvents in supercritical fluid extraction methods.

Any other suitable method may be used to obtain the desired oil extract fractions, including, but not limited to, mechanical pressing. Mechanical pressing, also known as expeller pressing, removes oil through the use of continuously driven screws that crush the seed or other oil-bearing material into a pulp from which the oil is expressed. Friction created in the process can generate
20   temperatures between about 50°C and 90°C, or external heat may be applied. Cold pressing generally refers to mechanical pressing conducted at a temperature of 40°C or less with no external heat applied.

The yield of oil extract that may be obtained from a plant material may depend upon any number of factors, but primarily upon the oil content of the plant material. For example, a typical
25   oil content of vetch (hexane extraction, dry basis) is approximately 4 to 5 wt. %, while that for barley is approximately 6 to 7.5 wt. %, and that for alfalfa is approximately 2 to 4.2 wt.%.

Thermal Stabilizers

In a preferred embodiment, the formulation may also contain jojoba oil as an additional component. It is a liquid that has antioxidant characteristics and is capable of withstanding very
30   high temperatures without losing its antioxidant abilities. Jojoba oil is a liquid wax ester mixture extracted from ground or crushed seeds from shrubs native to Arizona, California and northern Mexico. The source of jojoba oil is the Simmondsia chinensis shrub, commonly called the jojoba plant. It is a woody evergreen shrub with thick, leathery, bluish-green leaves and dark brown, nutlike fruit. Jojoba oil may be extracted from the fruit by conventional pressing or solvent
35   extraction methods. The oil is clear and golden in color. Jojoba oil is composed almost completely of wax esters of monounsaturated, straight-chain acids and alcohols with high molecular weights (C16-C26). Jojoba oil is typically defined as a liquid wax ester with the generic formula RCOOR",

wherein RCO represents oleic acid (C18), eicosanoic acid (C20) and/or erucic acid (C22), and wherein -OR" represents eicosenyl alcohol (C20), docosenyl alcohol (C22) and/or tetrasenyl alcohol (C24) moieties. Pure esters or mixed esters having the formula RCOOR", wherein R is a C20-C22 alk(en)yl group and wherein R" is a C20-C22 alk(en)yl group, may be suitable substitutes, in part or in whole, for jojoba oil. Acids and alcohols including monounsaturated straight-chain alkenyl groups are most preferred.

While the jojoba oil is preferred in many embodiments, in other embodiments it may be desirable to substitute, in whole or in part, another component, including, but not limited to, oils that are known for their thermal stability, such as, peanut oil, cottonseed oil, rape seed oil, macadamia oil, avocado oil, palm oil, palm kernel oil, castor oil, all other vegetable and nut oils, all animal oils including mammal oils (e.g., whale oils) and fish oils, and combinations and mixtures thereof. In preferred embodiments, the oil may be alkoxylated, for example, methoxylated or ethoxylated. Alkoxylation is preferably conducted on medium chain oils, such as castor oil, macadamia nut oil, cottonseed oil; and the like. Alkoxylation may offer benefits in that it may permit coupling of oil/water mixtures in a fuel, resulting in a potential reduction in nitrogen oxides and/or particulate matter emissions upon combustion of the fuel.

In preferred embodiments, these other oils are substituted for jojoba oil on a 1:1 volume ratio basis, in either a partial substitution or complete substitution. In other embodiments it may be preferred to substitute the other oil for jojoba oil at a volume ration greater than or less than a 1:1 volume ratio. In a preferred embodiment, cottonseed oil, either purified or merely extracted or crushed from cottonseed, squalene, or squalane are substituted on a 1:1 volume ratio basis for a portion or an entire volume of jojoba oil.

Although jojoba oil is preferred for used in many of the formulations of the preferred embodiments, in certain formulations it may be preferred to substitute one or more different thermal stabilizers for jojoba oil, either in whole or in part. Suitable thermal stabilizers as known in the art include liquid mixtures of alkyl phenols, including 2-tert-butylphenol, 2,6-di-tert-butylphenol, 2-tert-butyl-4-n-butylphenol, 2,4,6-tri-tert-butylphenol, and 2,6-di-tert-butyl-4-n-butylphenol which are suited for use as stabilizers for middle distillate fuels (US 5,076,814 and U.S. 5,024,775 to Hanlon, et al.). Other commercially available hindered phenolic antioxidants that also exhibit a thermal stability effect include 2,6-di-t-butyl-4-methylphenol; 2,6-di-t-butylphenol; 2,2'-methylene-bis(6-t-butyl-4-methylphenol); n-octadecyl 3-(3,5-di-t-butyl-4-hydroxyphenyl) propionate; 1,1,3-tris(3-t-butyl-6-methyl-4-hydroxyphenyl) butane; pentaerythrityl tetrakis[3-(3,5-di-t-butyl-4-hydroxyphenyl) propionate]; di-n-octadecyl(3,5-di-t-butyl-4-hydroxybenzyl)phosphonate; 2,4,6-tris(3,5-di-t-butyl-4-hydroxybenzyl) mesitylene; and tris(3,5-di-t-butyl-4-hydroxybenzyl)isocyanurate (U.S. 4,007,157, U.S. 3,920,661).

Other thermal stabilizers include: pentaerythritol co-esters derived from pentaerythritol, (3-alkyl-4-hydroxyphenyl)-alkanoic acids and alkylthioalkanoic acids or lower alkyl esters of such

acids which are useful as stabilizers of organic material normally susceptible to oxidative and/or thermal deterioration. (U.S. 4,806,675 and U.S. 4,734,519 to Dunski, et al.); the reaction product of malonic acid, dodecyl aldehyde and tallowamine (U.S. 4,670,021 to Nelson, et al.); hindered phenyl phosphites (U.S. 4,207,229 to Spivack); hindered piperidine carboxylic acids and metal salts thereof (U.S. 4,191,829 and U.S. 4,191,682 to Ramey, et al.); acylated derivatives of 2,6-dihydroxy-9-azabicyclo[3.3.1]nonane (U.S. 4,000,113 to Stephen); bicyclic hindered amines (U.S. 3,991,012 to Ramey, et al.); sulfur containing derivatives of dialkyl-4-hydroxyphenyltriazine (U.S. 3,941,745 to Dexter, et al.); bicyclic hindered amino acids and metal salts thereof (U.S. 4,051,102 to Ramey , et al.); trialkylsubstituted hydroxybenzyl malonates (U.S. 4,081,475 to Spivack); hindered piperidine carboxylic acids and metal salts thereof (U.S. 4,089,842 to Ramey , et al.); pyrrolidine dicarboxylic acids and esters (U.S. 4,093,586 to Stephen); metal salts of N,N-disubstituted β-alanines (U.S. 4,077,941 to Stephen , et al.); hydrocarbyl thioalkylene phosphites (U.S. 3,524,909); hydroxybenzyl thioalkylene phosphites (U.S. 3,655,833); and the like.

Certain compounds are capable of performing as both antioxidants and as thermal stabilizers. Therefore, in certain embodiments it may be preferred to prepare formulations containing as additional components a hydrophobic plant oil extract in combination with a single compound that provides both a thermal stability and antioxidant effect, rather than two different compounds, one providing thermal stability and the other antioxidant activity. Examples of compounds known in the art as providing some degree of both oxidation resistance and thermal stability include diphenylamines, dinaphthylamines, and phenylnaphthylamines, either substituted or unsubstituted, e.g., N,N'-diphenylphenylenediamine, p-octyldiphenylamine, p,p-dioctyldiphenylamine, N-phenyl-1-naphthylamine, N-phenyl-2-naphthylamine, N-(p-dodecyl)phenyl-2-naphthylamine, di-1-naphthylamine, and di-2naphthylamine; phenothazines such as N-alkylphenothiazines; imino(bisbenzyl); and hindered phenols such as 6-(t-butyl)phenol, 2,6-di-(t-butyl)phenol, 4-methyl-2,6-di-(t-butyl) phenol, 4,4'-methylenebis(-2,6-di-(t-butyl)phenol), and the like.

Certain lubricating fluid base stocks are known in the art to exhibit high thermal stability. Such base stocks may be capable of imparting thermal stability to the formulations of preferred embodiments, and as such may be substituted, in part or in whole, for jojoba oil. Suitable base stocks include polyalphaolefins, dibasic acid esters, polyol esters, alkylated aromatics, polyalkylene glycols, and phosphate esters.

Polyalphaolefins are hydrocarbon polymers that contain no sulfur, phosphorus, or metals. Polyalphaolefins have good thermal stability, but are typically used in conjunction with a suitable antioxidant. Dibasic acid esters also exhibit good thermal stability, but are usually also used in combination with additives for resistance to hydrolysis and oxidation.

Polyol esters include molecules containing two or more alcohol moieties, such as trimethylolpropane, neopentylglycol, and pentaerythritol esters. Synthetic polyol esters are the

reaction product of a fatty acid derived from either animal or plant sources and a synthetic polyol. Polyol esters have excellent thermal stability and may resist hydrolysis and oxidation better than other base stocks. Naturally occurring triglycerides or vegetable oils are in the same chemical family as polyol esters. However, polyol esters tend to be more resistant to oxidation than such

5   oils. The oxidation instabilities normally associated with vegetable oils are generally due to a high content of linoleic and linolenic fatty acids. Moreover, the degree of unsaturation (or double bonds) in the fatty acids in vegetable oils correlates with sensitivity to oxidation, with a greater number of double bonds resulting in a material more sensitive to and prone to rapid oxidation.

Trimethylolpropane esters may include mono, di, and tri esters. Neopentyl glycol esters

10 may include mono and di esters. Pentaerythritol esters include mono, di, tri, and tetra esters. Dipentaerythritol esters may include up to six ester moieties. Preferred esters are typically of those of long chain monobasic fatty acids. Esters of C20 or higher acids are preferred, e.g., gondoic acid, eicosadienoic acid, eicosatrienoic acid, eicosatetraenoic acid, eicosapentanoic acid, arachidic acid, arachidonic acid, behenic acid, erucic acid, docosapentanoic acid, docosahexanoic acid, or

15 ligniceric acid. However in certain embodiments, esters of C18 or lower acids may be preferred, e.g., butyric acid, caproic acid, caprylic acid, capric acid, lauric acid, myristoleic acid, myristic acid, pentadecanoic acid, palmitic acid, palmitoleic acid, hexadecadienoic acid, hexadecatienoic acid, hexadecatetraenoic acid, margaric acid, margroleic acid, stearic acid, linoleic acid, octadecatetraenoic acid, vaccenic acid, or linolenic acid. In certain embodiments, it may be

20 preferred to esterify the pentaerythritol with a mixture of different acids.

Alkylated aromatics are formed by the reaction of olefins or alkyl halides with aromatic compounds, such as benzene. Thermal stability is similar to that of polyalphaolefins, and additives are typically used to provide oxidative stability. Polyalkylene glycols are polymers of alkylene oxides exhibiting good thermal stability, but are typically used in combination with additives to

25 provide oxidation resistance. Phosphate esters are synthesized from phosphorus oxychloride and alcohols or phenols and also exhibit good thermal stability.

In certain embodiments, it may be preferred to prepare formulations containing jojoba oil in combination with other vegetable oils. For example, it has been reported that crude meadowfoam oil resists oxidative destruction nearly 18 times longer than the most common vegetable oil,

30 namely, soybean oil. Meadowfoam oil may be added in small amounts to other oils, such as triolein oil, jojoba oil, and castor oil, to improve their oxidative stability. Crude meadowfoam oil stability could not be attributed to common antioxidants. One possible explanation for the oxidative stability of meadowfoam oil may be its unusual fatty acid composition. The main fatty acid from meadowfoam oil is 5-eicosenoic acid, which was found to be nearly 5 times more stable to

35 oxidation than the most common fatty acid, oleic acid, and 16 times more stable than other monounsaturated fatty acids. See "Oxidative Stability Index of Vegetable Oils in Binary Mixtures

with Meadowfoam Oil," Terry, et al., United States Department of Agriculture, Agricultural Research Service, 1997.

Detergent Additives - Carburetor deposits may form in the throttle body and plate, idle air circuit, and in the metering orifices and jets. These deposits are a combination of contaminants from dust and engine exhaust, held together by gums formed from unsaturated hydrocarbons in the fuel. They can alter the air/fuel ratio, cause rough idling, increased fuel consumption, and increased exhaust emissions. Carburetor detergents can prevent deposits from forming and remove deposits already formed. Detergents used for this application are amines in the 20-60 ppm dosage range.

Fuel injectors are very sensitive to deposits that can reduce fuel flow and alter the injector spray pattern. These deposits can make vehicles difficult to start, cause severe driveability problems, and increase fuel consumption and exhaust emissions. Fuel injector deposits are formed at higher temperatures than carburetor deposits and are therefore more difficult to deal with. The amines used for carburetor deposits are somewhat effective but are typically used at roughly the 100 ppm dosage level. At this level, the amine detergent can actually cause the formation of inlet manifold and valve deposits. Polymeric dispersants with higher thermal stability than the amine detergents have been used to overcome this problem. These are used at dosages in the range of 20 to 600 ppm. These same additives are also effective for inlet manifold and valve deposit control. Inlet manifold and valve deposits have the same effect on driveability, fuel consumption, and exhaust emissions as carburetor and engine deposits. The effect of detergent and dispersant additives on engines with existing deposits may require several tanks of gasoline, especially if the additives are used at a low dosage rate.

Combustion chamber deposits can cause an increase in the octane number requirement for vehicles as they accumulate miles. These deposits accumulate in the end-gas zone and injection port area. They are thermal insulators and so can become very hot during engine operation. The metallic surfaces conduct heat away and remain relatively cool. The hot deposits can cause pre-ignition and misfire leading to the need for a higher-octane fuel. Polyetheramine and other proprietary additives are known to reduce the magnitude of combustion chamber deposits. Reduction in the amount of combustion chamber deposits has been shown to reduce NO_x emissions.

Any of a number of different types of suitable detergent additives can be included in diesel fuel compositions of various embodiments. These detergents include succinimide detergent/dispersants, long-chain aliphatic polyamines, long-chain Mannich bases, and carbamate detergents. Desirable succinimide detergent/dispersants for use in gasolines are prepared by a process that includes reacting an ethylene polyamine such as diethylene triamine or triethylene tetramine with at least one acyclic hydrocarbyl substituted succinic acylating agent. The substituent of such acylating agent is characterized by containing an average of about 50 to about 100 (preferably about 50 to about 90 and more preferably about 64 to about 80) carbon atoms. Additionally, the acylating agent has an acid number in the range of about 0.7 to about 1.3 (for

example, in the range of 0.9 to 1.3, or in the range of 0.7 to 1.1), more preferably in the range of 0.8 to 1.0 or in the range of 1.0 to 1.2, and most preferably about 0.9. The detergent/dispersant contains in its molecular structure in chemically combined form an average of from about 1.5 to about 2.2 (preferably from 1.7 to 1.9 or from 1.9 to 2.1, more preferably from 1.8 to 2.0, and most preferably about 1.8) moles of the acylating agent per mole of the polyamine. The polyamine can be a pure compound or a technical grade of ethylene polyamines that typically are composed of linear, branched and cyclic species.

The acyclic hydrocarbyl substituent of the detergent/dispersant is preferably an alkyl or alkenyl group having the requisite number of carbon atoms as specified above. Alkenyl substituents derived from poly-olefin homopolymers or copolymers of appropriate molecular weight (for example, propene homopolymers, butene homopolymers, C_3 and C_4 olefin copolymers, and the like) are suitable. Most preferably, the substituent is a polyisobutenyl group formed from polyisobutene having a number average molecular weight (as determined by gel permeation chromatography) in the range of 700 to 1200, preferably 900 to 1100, most preferably 940 to 1000. The established manufacturers of such polymeric materials are able to adequately identify the number average molecular weights of their own polymeric materials. Thus in the usual case the nominal number average molecular weight given by the manufacturer of the material can be relied upon with considerable confidence.

Acyclic hydrocarbyl-substituted succinic acid acylating agents and methods for their preparation and use in the formation of succinimide are well known to those skilled in the art and are extensively reported in the literature. See, for example, U.S. Pat. No. 3,018,247.

Use of fuel-soluble long chain aliphatic polyamines as induction cleanliness additives in distillate fuels is described, for example, in U.S. Pat. No. 3,438,757.

Use of fuel-soluble Mannich base additives formed from a long chain alkyl phenol, formaldehyde (or a formaldehyde precursor thereof), and a polyamine to control induction system deposit formation in internal combustion engines is described, for example, in U.S. Pat. No. 4,231,759.

Carbamate fuel detergents are compositions which contain polyether and amine groups joined by a carbamate linkage. Typical compounds of this type are described in U.S. Pat. No. 4,270,930. A preferred material of this type is commercially available from Chevron Oronite Company LLC of Houston, TX as OGA-480™ additive.

Driveability Additives - For gasoline powered engines, these include anti-knock, anti-run-on, anti-pre-ignition, and anti-misfire additives that directly effect the combustion process. Anti-knock additives include lead alkyls that are no longer used in the United States. These and other metallic anti-knock additives are typically used at dosages of roughly 0.2 g metal/liter of fuel (or about 0.1 wt % or 1000 ppm). A typical octane number enhancement at this dosage level is 3 units for both Research Octane Number (RON) and Motor Octane Number (MON). A number of

organic compounds are also known to have anti-knock activity. These include aromatic amines, alcohols, and ethers that can be employed at dosages in the 1000 ppm range. These additives work by transferring hydrogen to quench reactive radicals. Oxygenates such as methanol and MTBE also increase octane number but these are used at such high dosages that they are not really additives but

5   blend components. Pre-ignition is generally caused by the presence of combustion chamber deposits and is treated using combustion chamber detergents and by raising octane number. Driveability additives may also be employed for diesel engines.

Antiwear Agents - The diesel fuel compositions of various embodiments advantageously contain one or more antiwear agents. Preferred antiwear agents include long chain primary amines

10   incorporating an alkyl or alkenyl radical having 8 to 50 carbon atoms. The amine to be employed may be a single amine or may consist of mixtures of such amines. Examples of long chain primary amines which can be used in the preferred embodiments are 2-ethylhexyl amine, n-octyl amine, n-decyl amine, dodecyl amine, oleyl amine, linolylamine, stearyl amine, eicosyl amine, triacontyl amine, pentacontyl amine and the like. A particularly effective amine is oleyl amine obtainable

15   from Akzo Nobel Surface Chemistry LLC of Chicago, IL under the name ARMEEN® O or ARMEEN® OD. Other suitable amines which are generally mixtures of aliphatic amines include ARMEEN® T and ARMEEN® TD, the distilled form of ARMEEN® T which contains a mixture of 0-2% of tetradecyl amine, 24% to 30% of hexadecyl amine, 25% to 28% of octadecyl amine and 45% to 46% of octadecenyl amine. ARMEEN® T and ARMEEN® TD are derived from tallow

20   fatty acids. Lauryl amine is also suitable, as is ARMEEN® 12D obtainable from the supplier indicated above. This product is about 0-2% of decylamine, 90% to 95% dodecylamine, 0-3% of tetradecylamine and 0-1% of octadecenylamine. Amines of the types indicated to be useful are well known in the art and may be prepared from fatty acids by converting the acid or mixture of acids to its ammonium soap, converting the soap to the corresponding amide by means of heat, further

25   converting the amide to the corresponding nitrile and hydrogenating the nitrile to produce the amine. In addition to the various amines described, the mixture of amines derived from soya fatty acids also falls within the class of amines above described and is suitable for use according to this invention. It is noted that all of the amines described above as being useful are straight chain, aliphatic primary amines. Those amines having 16 to 18 carbon atoms per molecule and being

30   saturated or unsaturated are particularly preferred.

Other preferred antiwear agents include dimerized unsaturated fatty acids, preferably dimers of a comparatively long chain fatty acid, for example one containing from 8 to 30 carbon atoms, and may be pure, or substantially pure, dimers. Alternatively, and preferably, the material sold commercially and known as "dimer acid" may be used. This latter material is prepared by

35   dimerizing unsaturated fatty acid and consists of a mixture of monomer, dimer and trimer of the acid. A particularly preferred dimer acid is the dimer of linoleic acid.

Antioxidants - Various compounds known for use as oxidation inhibitors can be utilized in fuel formulations of various embodiments. These include phenolic antioxidants, amine antioxidants, sulfurized phenolic compounds, and organic phosphites, among others. For best results, the antioxidant includes predominately or entirely either (1) a hindered phenol antioxidant such as 2,6-di-tert-butylphenol, 4-methyl-2,6-di-tert-butylphenol, 2,4-dimethyl-6-tert-butylphenol, 4,4'-methylenebis(2,6-di-tert-butylphenol), and mixed methylene bridged polyalkyl phenols, or (2) an aromatic amine antioxidant such as the cycloalkyl-di-lower alkyl amines, and phenylenediamines, or a combination of one or more such phenolic antioxidants with one or more such amine antioxidants. Particularly preferred are combinations of tertiary butyl phenols, such as 2,6-di-tert-butylphenol, 2,4,6-tri-tert-butylphenol and o-tert-butylphenol. Also useful are N,N'-di-lower-alkyl phenylenediamines, such as N,N'-di-sec-butyl-p-phenylenediamine, and its analogs, as well as combinations of such phenylenediamines and such tertiary butyl phenols.

Demulsifiers - Demulsifiers are molecules that aid the separation of oil from water usually at very low concentrations. They prevent formation of a water and oil mixture. A wide variety of demulsifiers are available for use in the fuel formulations of various embodiments, including, for example, organic sulfonates, polyoxyalkylene glycols, oxyalkylated phenolic resins, and like materials. Particularly preferred are mixtures of alkylaryl sulfonates, polyoxyalkylene glycols and oxyalkylated alkylphenolic resins, such as are available commercially from Baker Petrolite Corporation of Sugar Land, TX under the TOLAD® trademark. Other known demulsifiers can also be used.

Corrosion Inhibitors - A variety of corrosion inhibitors are available for use in the fuel formulations of various embodiments. Use can be made of dimer and trimer acids, such as are produced from tall oil fatty acids, oleic acid, linoleic acid, or the like. Products of this type are currently available from various commercial sources, such as, for example, the dimer and trimer acids sold under the EMPOL® trademark by Cognis Corporation of Cincinnati, OH. Other useful types of corrosion inhibitors are the alkenyl succinic acid and alkenyl succinic anhydride corrosion inhibitors such as, for example, tetrapropenylsuccinic acid, tetrapropenylsuccinic anhydride, tetradecenylsuccinic acid, tetradecenylsuccinic anhydride, hexadecenylsuccinic acid, hexadecenylsuccinic anhydride, and the like. Also useful are the half esters of alkenyl succinic acids having 8 to 24 carbon atoms in the alkenyl group with alcohols such as the polyglycols.

Also useful are the aminosuccinic acids or derivatives. Preferably a dialkyl ester of an aminosuccinic acid is used containing an alkyl group containing 15-20 carbon atoms or an acyl group which is derived from a saturated or unsaturated carboxylic acid containing 2-10 carbon atoms. Most preferred is a dialkylester of an aminosuccinic acid.

Metal Deactivators - If desired, the fuel compositions may contain a conventional type of metal deactivator of the type having the ability to form complexes with heavy metals such as copper

and the like. Typically, the metal deactivators used are gasoline soluble N,N'-disalicylidene-1,2-alkanediamines or N,N'-disalicylidene-1,2-cycloalkanediamines, or mixtures thereof. Examples include N,N'-disalicylidene-1,2-ethanediamine, N,N'-disalicylidene-1,2-propanediamine, N,N'-disalicylidene-1,2-cyclo-hexanediamine, and N,N''-disalicylidene-N'-methyl-dipropylene-triamine.

The various additives that can be included in the diesel compositions of this invention are used in conventional amounts. The amounts used in any particular case are sufficient to provide the desired functional property to the fuel composition, and such amounts are well known to those skilled in the art.

Thermal Stabilizers - Thermal stabilizers such as Octel Starreon high temperature fuel oil stabilizer FOA-81™, or other such additives may also be added to the fuel formulation.

Carrier fluids - Substances suitable for use as carrier fluids include, but are not limited to, mineral oils, vegetable oils, animal oils, and synthetic oils. Suitable mineral oils may be primarily paraffinic, naphthenic, or aromatic in composition. Animal oils include tallow and lard. Vegetable oils may include, but are not limited to, rapeseed oil, soybean oil, peanut oil, corn oil, sunflower oil, cottonseed oil, coconut oil, olive oil, wheat germ oil, flaxseed oil, almond oil, safflower oil, castor oil, and the like. Synthetic oils may include, but are not limited to, alkyl benzenes, polybutylenes, polyisobutylenes, polyalphaolefins, polyol esters, monoesters, diesters (adipates, sebacates, dodecanedioates, phthalates, dimerates), and triesters.

Solvents - Solvents suitable for use in conjunction with the formulations of preferred embodiments are miscible and compatible with one or more components of the formulation. Preferred solvents include the aromatic solvents, such as benzene, toluene, o-xylene, m-xylene, p-xylene, and the like, as well as nonpolar solvents such as cyclohexanes, hexanes, heptanes, octanes, nonanes, and the like. Suitable solvents may also include the fuel to be additized, e.g., gasoline, Diesel 1, Diesel 2, and the like. Depending upon the material to be solvated, other liquids may also be suitable for use as solvents, such as oxygenates, carrier fluids, or even additives as enumerated herein.

Oxygenates - Oxygenates are added to gasoline to improve octane number and to reduce emissions of CO. These include various alcohols and ethers that are typically blended with gasoline to produce an oxygen content typically of up to about 2 weight percent, although higher concentrations may be desirable in certain embodiments. The CO emissions benefit appears to be a function of fuel oxygen level and not of oxygenate chemical structure. Because oxygenates have a lower heating value than gasoline, volumetric fuel economy (miles per gallon) is lower for fuels containing these components. However, at typical blend levels the effect is so small that only very precise measurements can detect it. Oxygenates are not known to effect emissions of NO_x or hydrocarbon.

In certain embodiments, it may be preferred to add one or more oxygenates to the fuel. Oxygenates are hydrocarbons that contain one or more oxygen atoms. The primary oxygenates are

alcohols and ethers, including: methanol, fuel ethanol, methyl tertiary butyl ether (MTBE), ethyl tertiary butyl ether (ETBE), diisopropyl ether (DIPE), and tertiary amyl methyl ether (TAME).

Microencapsulated Beta-Carotene

5   In certain of the preferred embodiments, it may be desirable to encapsulate the beta-carotene or other carotenoid(s) and/or carotene(s) prior to incorporation into the fuel additive, diesel fuel formulation, or other fuel formulation. Microencapsulation is an effective technique to avoid undesired chemical interaction between additives and ambient oxygen and other substances. Encapsulated or otherwise preserved beta-carotene may resist oxidation and other degradative effects that may inhibit its effectiveness as a cetane improver or other type of fuel additive (e.g., an

10   emission reducing additive, a fuel economy additive, and the like). Accordingly, an antioxidant or other additive, such as ethoxyquin, may not be necessary to stabilize the beta-carotene such that it remains effective as a cetane improver under ambient conditions.

In a preferred embodiment, the beta-carotene and optionally other additive components are entrapped into lecithin microcapsules or nanoparticles. Other preferred shell materials include fuel-

15   soluble polymers or fuel-miscible polymers. The microcapsules' shells block undesired reactions by substantially preventing direct contact of the additive contained within and the fuel or atmosphere. The microencapsulated additives may also provide long-term controlled release of additives to the fuel at a preselected concentration.

Microencapsulation techniques generally involve the coating of small solid particles, liquid

20   droplets, or gas bubbles with a thin film of a material, the material providing a protective shell for the contents of the microcapsule. Microcapsules suitable for use in the preferred embodiments may be of any suitable size, typically from about 1 μm or less to about 1000 μm or more, preferably from about 2 μm to about 50, 60, 70, 80, 90, 100, 200, 300, 400, 500, 600, 700, 800, or 900 μm, and more preferably from about 3, 4, 5, 6, 7, 8, or 9 μm to about 10, 15, 20, 25, 30, 35, 40 or 45

25   μm. In certain embodiments, it may be preferred to use nanometer-sized microcapsules. Such microcapsules may range from about 10 nm or less up to less than about 1000 nm (1 μm), preferably from about 10, 15, 20, 25, 30, 35, 40, 45, 50, 60, 70, 80, or 90 nm up to about 100, 200, 300, 400, 500, 600, 700, 800, or 900 nm.

While in most embodiments liquid phase beta-carotene or another liquid additive substance

30   is encapsulated, in certain embodiments it may be preferred to incorporate a solid substance. Solid containing microcapsules may be prepared using conventional methods well known in the art of microcapsule formation, and such microcapsules may be incorporated into the additive packages and fuels of preferred embodiments.

Microcapsule Components

35   The microcapsules of preferred embodiments contain a filling material. The filling material is typically one or more carotenes, carotenoids, their derivatives and precursors, or long chain

unsaturated compounds, optionally in combination with other substances, such as a beta-carotene stabilizer, e.g., ethoxyquin. The filling material is encapsulated within the microcapsule by a shell material.

Typical shell materials may include, but are not limited to, gum arabic, gelatin,
5 ethylcellulose, polyurea, polyamide, aminoplasts, maltodextrins, and hydrogenated vegetable oil. While any suitable shell material may be used in the preferred embodiments, it is generally preferred to use shell materials approved for use in food or pharmaceutical applications. Gelatin is particularly preferred because of its low cost, biocompatibility, and the ease with which gelatin shell microcapsules may be prepared. In certain embodiments, however, other shell materials may
10 be preferred. The optimum shell material may depend, for example, upon the particle or droplet size and size distribution of the filling material, the shape of the filling material particles, compatibility with the filling material, stability of the filling material, and the rate of release of the filling material from the microcapsule. If a hydrophilic substance is utilized as a shell material, it may be desirable to utilize a dispersing or emulsifying agent to ensure uniform distribution of the
15 microcapsules in the fuel additive package or additized fuel.

Microencapsulation Processes

A variety of encapsulation methods may be used to prepare the microcapsules of preferred embodiments. These methods include gas phase and vacuum processes wherein a coating is sprayed or otherwise deposited on the filler material particles so as to form a shell, or processes
20 wherein a liquid is sprayed into a gas phase and is subsequently solidified to produce microcapsules. Suitable methods also include emulsion and dispersion methods wherein the microcapsules are formed in the liquid phase in a reactor.

Spray Drying

Encapsulation by spray drying involves spraying a concentrated solution of shell material
25 containing filler material particles or a dispersion of immiscible liquid filler material into a heated chamber where rapid desolvation occurs. Any suitable solvent system may be used. Spray drying is commonly used to prepare microcapsules including shell materials such as, for example, gelatin, hydrolyzed gelatin, gum arabic, modified starch, maltodextrins, sucrose, or sorbitol. When an aqueous solution of shell material is used, the filler material typically includes a hydrophobic liquid
30 or water-immiscible oil. Dispersants and/or emulsifiers may be added to the concentrated solution of shell material. Relatively small microcapsules may be prepared by spray drying methods, e.g., from less than about 1 μm to greater than about 50 μm. The resulting particles may include individual particles as well as aggregates of individual particles. The amount of filler material that may be encapsulated using spray drying techniques is typically from less than about 20 wt. % of the
35 microcapsule to more than 60 wt. % of the microcapsule. The process is preferred because of its low cost compared to other methods, and has wide utility in preparing microcapsules. The method may not be preferred for preparing heat sensitive materials.

In another variety of spray drying, chilled air rather than desolvation is used to solidify a molten mixture of shell material containing filler material in the form of particles or an immiscible liquid. Various fats, waxes, fatty alcohols, and fatty acids are typically used as shell materials in such an encapsulation method. The method is generally preferred for preparing microcapsules having water-insoluble shells.

Fluidized-Bed Microencapsulation

Encapsulation using fluidized bed technology involves spraying a liquid shell material, generally in solution or melted form, onto solid particles suspended in a stream of gas, typically heated air, and the particles thus encapsulated are subsequently cooled. Shell materials commonly used include, but are not limited to, colloids, solvent-soluble polymers, and sugars. The shell material may be applied to the particles from the top of the reactor, or may be applied as a spray from the bottom of the reactor, e.g., as in the Wurster process. The particles are maintained in the reactor until a desired shell thickness is achieved. Fluidized bed microencapsulation is commonly used for preparing encapsulated water-soluble ingredients. The method is particularly suitable for coating irregularly shaped particles. Fluidized bed encapsulation is typically used to prepare microcapsules larger than about 100 μm, however smaller microcapsules may also be prepared.

Complex Coacervation

A pair of oppositely charged polyelectrolytes capable of forming a liquid complex coacervate (namely, a mass of colloidal particles that are bound together by electrostatic attraction) can be used to form microcapsules by complex coacervation. A preferred polyanion is gelatin, which is capable of forming complexes with a variety of polyanions. Typical polyanions include gum arabic, polyphosphate, polyacrylic acid, and alginate. Complex coacervation is used primarily to encapsulate water-immiscible liquids or water-insoluble solids. The method is not suitable for use with water soluble substances, or substances sensitive to acidic conditions.

In the complex coacervation of gelatin with gum arabic, a water insoluble filler material is dispersed in a warm aqueous gelatin emulsion, and then gum arabic and water are added to this emulsion. The pH of the aqueous phase is adjusted to slightly acidic, thereby forming the complex coacervate which adsorbs on the surface of the filler material. The system is cooled, and a cross-linking agent, such as glutaraldehyde, is added. The microcapsules may optionally be treated with urea and formaldehyde at low pH so as to reduce the hydrophilicity of the shell, thereby facilitating drying without excessive aggregate formation. The resulting microcapsules may then be dried to form a powder.

Polymer-Polymer Incompatibility

Microcapsules may be prepared using a solution containing two liquid polymers that are incompatible, but soluble in a common solvent. One of the polymers is preferentially absorbed by the filler material. When the filler material is dispersed in the solution, it is spontaneously coated by a thin film of the polymer that is preferentially absorbed. The microcapsules are obtained by

either crosslinking the absorbed polymer or by adding a nonsolvent for the polymer to the solution. The liquids are then removed to obtain the microcapsules in the form of a dry powder.

Polymer-polymer incompatibility encapsulation can be carried out in aqueous or nonaqueous media. It is typically used for preparing microcapsules containing polar solids with 5 limited water solubility. Suitable shell materials include ethylcellulose, polylactide, and lactide-glycolide copolymers. Microcapsules prepared by polymer-polymer incompatibility encapsulation tend to be smaller than microcapsules prepared by other methods, and typically have diameters of 100 μm or less.

Interfacial Polymerization

10 Microcapsules may be prepared by conducting polymerization reactions at interfaces in a liquid. In one such type of microencapsulation method, a dispersion of two immiscible liquids is prepared. The dispersed phase forms the filler material. Each phase contains a separate reactant, the reactants capable of undergoing a polymerization reaction to form a shell. The reactant in the dispersed phase and the reactant in a continuous phase react at the interface between the dispersed 15 phase and the continuous phase to form a shell. The reactant in the continuous phase is typically conducted to the interface by a diffusion process. Once reaction is initiated, the shell eventually becomes a barrier to diffusion and thereby limits the rate of the interfacial polymerization reaction. This may affect the morphology and uniformity of thickness of the shell. Dispersants may be added to the continuous phase. The dispersed phase can include an aqueous or a nonaqueous solvent. The 20 continuous phase is selected to be immiscible in the dispersed phase.

Typical polymerization reactants may include acid chlorides or isocyanates, which are capable of undergoing a polymerization reaction with amines or alcohols. The amine or alcohol is solubilized in the aqueous phase in a nonaqueous phase capable solubilizing the amine or alcohol. The acid chloride or isocyanate is then dissolved in the water- (or nonaqueous solvent-) immiscible 25 phase. Similarly, solid particles containing reactants or having reactants coated on the surface may be dispersed in a liquid in which the solid particles are not substantially soluble. The reactants in or on the solid particles then react with reactants in the continuous phase to form a shell.

In another type of microencapsulation by interfacial polymerization, commonly referred to as *in situ* encapsulation, a filler material in the form of substantially insoluble particles or in the 30 form of a water immiscible liquid is dispersed in an aqueous phase. The aqueous phase contains urea, melamine, water-soluble urea-formaldehyde condensate, or water-soluble urea-melamine condensate. To form a shell encapsulating the filler material, formaldehyde is added to the aqueous phase, which is heated and acidified. A condensation product then deposits on the surface of the dispersed core material as the polymerization reaction progresses. Unlike the interfacial 35 polymerization reaction described above, the method may be suitable for use with sensitive filler materials since reactive agents do not have to be dissolved in the filler material. In a related *in situ* polymerization method, a water-immiscible liquid or solid containing a water-immiscible vinyl

monomer and vinyl monomer initiator is dispersed in an aqueous phase. Polymerization is initiated by heating and a vinyl shell is produced at the interface with the aqueous phase.

Gas Phase Polymerization

Microcapsules may be prepared by exposing filler material particles to a gas capable of undergoing polymerization on the surface of the particles. In one such method, the gas comprises p-xylene dimers that polymerize on the surface of the particle to form a poly(p-xylene) shell. Specialized coating equipment may be necessary for conducting such coating methods, making the method more expensive than certain liquid phase encapsulation methods. Also, the filler material to be encapsulated is preferably not sensitive to the reactants and reaction conditions.

Solvent Evaporation

Microcapsules may be prepared by removing a volatile solvent from an emulsion of two immiscible liquids, e.g., an oil-in-water, oil-in-oil, or water-in-oil-in-water emulsion. The material that forms the shell is soluble in the volatile solvent. The filler material is dissolved, dispersed, or emulsified in the solution. Suitable solvents include methylene chloride and ethyl acetate. Solvent evaporation is a preferred method for encapsulating water soluble filler materials, for example, polypeptides. When such water-soluble components are to be encapsulated, a thickening agent is typically added to the aqueous phase, then the solution is cooled to gel the aqueous phase before the solvent is removed. Dispersing agents may also be added to the emulsion prior to solvent removal. Solvent is typically removed by evaporation at atmospheric or reduced pressure. Microcapsules less than 1 μm or over 1000 μm in diameter may be prepared using solvent evaporation methods.

Centrifugal Force Encapsulation

Microencapsulation by centrifugal force typically utilizes a perforated cup containing an emulsion of shell and filler material. The cup is immersed in an oil bath and spun at a fixed rate, whereby droplets including the shell and filler material form in the oil outside the spinning cup. The droplets are gelled by cooling to yield oil-loaded particles that may be subsequently dried. The microcapsules thus produced are generally relatively large. In another variation of centrifugal force encapsulation referred to as rotational suspension separation, a mixture of filler material particles and either molten shell or a solution of shell material is fed onto a rotating disk. Coated particles are flung off the edge of the disk, where they are gelled or desolvated and collected.

Submerged Nozzle Encapsulation

Microencapsulation by submerged nozzle generally involves spraying a liquid mixture of shell and filler material through a nozzle into a stream of carrier fluid. The resulting droplets are gelled and cooled. The microcapsules thus produced are generally relatively large.

Desolvation

In desolvation or extractive drying, a dispersion filler material in a concentrated shell material solution or dispersion is atomized into a desolvation solvent, typically a water-miscible alcohol when an aqueous dispersion is used. Water-soluble shell materials are typically used,

including maltodextrins, sugars, and gums. Preferred desolvation solvents include water-miscible alcohols such as 2-propanol or polyglycols. The resulting microcapsules do not have a distinct filler material phase. Microcapsules thus produced typically contain less than about 15 wt. % filler material, but in certain embodiments may contain more filler material.

5   Liposomes

Liposomes are microparticles typically ranging in size from less than about 30 nm to greater than 1 mm. They consist of a bilayer of phospholipid encapsulating an aqueous space. The lipid molecules arrange themselves by exposing their polar head groups toward the aqueous phase, and the hydrophobic hydrocarbon groups adhere together in the bilayer forming close concentric

10   lipid leaflets separating aqueous regions. Medicaments can either be encapsulated in the aqueous space or entrapped between the lipid bilayers. Where the medicament is encapsulated depends upon its physiochemical characteristics and the composition of the lipid. Liposomes may slowly release any contained medicament through enzymatic hydrolysis of the lipid. Lecithin-based bilayered liposomes are particularly desirable encapsulants, due in part to the antioxidant properties

15   of lecithin.

Nanoparticles

Nanoparticles are small lipid vesicles, typically prepared from lecithin, in the range of nanometers. Liposomes and nanoparticles are of comparable size. Both occur in the range from 20 to 1000 nm in diameter. Whereas liposomes are composed of one or more bilayer membranes,

20   nanoparticles are formed by a single layered shell. Liposomes are typically filled with water-soluble or hydrophilic components and therefore are typical carriers for hydrophilic substances. In contrast, nanoparticles are filled with oleophilic or hydrophobic substances and lend themselves ideally as carriers for lipophilic agents.

High pressure homogenization using a microfluidizer is a sophisticated technology to

25   prepare lipid vesicles such as liposomes and nanoparticles. The method is easy to scale up and yields reproducible results. The homogenizer has a specially designed interaction chamber. In this chamber, the stream of the premixed components is first divided and then combined again at a particular angle. At this point, high shear and cavitation forces form the lipid vesicles at a pressure of up to 1200 bar. The technique of high pressure homogenization yields a 100% encapsulation of

30   dispersed oil in the vesicles.

Usually, multiple cycles through the interaction chamber are necessary to obtain a homogenous product. The mean droplet size and the size distribution are the main parameters to characterize nanoparticle preparations. They can be determined by photon correlation spectroscopy or by means of electron microscopy of samples prepared by freeze fracture.

35   The core of the particles can contain a wide variety of lipophilic agents, such as carotenes and carotenoids, as well as hydrophobic antioxidants. The chemical stability of these ingredients (against oxidation) can be enhanced by their encapsulation into nanoparticles. Nanoparticle

preparations can contain up to 40% of oil soluble components. The vesicle size is influenced by many parameters. Most important are homogenization pressure, concentration and type of lecithin, concentration and type of oil and the solvent concentration. Very small particles can only be achieved at a high ratio of phospholipid to oil.

5   Miscellaneous Microencapsulation Processes

While the microencapsulation methods described above are generally preferred for preparing the microcapsules of preferred embodiments, other suitable microencapsulation methods may also be used, as are known to those of skill in the art. Moreover, in certain embodiments, it may be desired to incorporate an unencapsulated carotene, carotenoid, or the like or other substance

10   directly into the fuel additive or additized fuel formulation. Alternatively, the additive or other substance may be incorporated into a solid matrix of a carrier substance. The microcapsules that are added to the fuel additive or additized fuel formulation may all be of the same type and contain the same additives or other substances, or may include a variety of types of microcapsules and/or encapsulated additives or other substances.

15   Spray Drying and Freeze Drying

Spray drying is widely used in industry as a method for the production of dry solids in either powder, granulate or agglomerate form from liquid feedstocks as solutions, emulsions and pumpable suspensions. Spray drying methods may be suitable for preparing solid particles containing carotenes, carotenoids, and the like. The apparatus used for spray drying typically

20   consists of a feed pump, rotary or nozzle atomizer, air heater, air disperser, drying chamber, and systems for exhaust air cleaning and powder recovery. In spray drying, a liquid feedstock is atomized into a spray of droplets and the droplets are contacted with hot air in a drying chamber. Evaporation of moisture from the droplets and formation of dry particles proceed under controlled temperature and airflow conditions. The powder, granulate or agglomerate formed is then

25   discharged from the drying chamber. In some cases, it may be necessary to continue the stirring or agitation of the solution during the spray drying process so that the composition made at the end of the spraying procedure is still well mixed. By adjusting the operating conditions and dryer design, the characteristics of the spray dried product can be determined.

Another preferred method for removing the solvent is freeze drying. Freeze drying consists

30   of three stages: pre-freezing, primary drying, and secondary drying. Before freeze drying may be initiated, the mixture to be freeze dried must be adequately pre-frozen, i.e., the material is completely frozen so that there are no pockets of unfrozen concentrated solute. In the case of aqueous mixtures of solutes that freeze at lower temperature than the surrounding water, the mixture must be frozen to the eutectic temperature. Once the mixture is adequately pre-frozen, then

35   the solvent is removed from the frozen mixture via sublimation in the primary drying step. After the primary drying step is completed, solvent may still be present in the mixture in bound form. To remove this bound solvent, continued drying is necessary to desorb the solvent from the product.

Preferred Methods for Encapsulating or Preserving Beta-Carotene

In preferred embodiments, beta-carotene may be encapsulated or preserved according to the methods described above. Beta-Carotene may be encapsulated by spray drying, drum drying, or freeze drying a mixture of beta-carotene in maltodextrin. It is generally preferred to utilize 0.5 g

5   beta-carotene per 1000 g aqueous solution of 40% maltodextrin 25 DE, and subject the mixture to homogenization prior to drying. Suitable methods of encapsulating beta-carotene in maltodextrin by freeze drying, spray drying, and /or drum drying are described in J. Food Sci. (1997), 62(6), 1158-1162; Crit. Rev. Food Sci. Nutr. (1998), 38(5), 381-396; and J. Food Process. Preserv. (1999), 23(1), 39-55.

10   Encapsulants other than maltodextrin for beta-carotene may also be employed. Such encapsulants include pullulan (water-soluble polysaccharide composed of glucose units that are polymerized in such a way as to make it viscous and impermeable to oxygen) and polyvinyl pyrrolidone of various molecular weights (PVP40 and PVP360, for example) as described in Food Chemistry (2000), 71(2), 199-206. Hydrolyzed starch may also be utilized as an encapsulant, as

15   described in J. Food Sci. (1995), 60(5), 1048-53.

Additive Concentrates

The cetane improving package can be added to the base fuel directly. Alternatively, the additive formulation may be provided in the form of an additive package that may be used to prepare an additized fuel. Optionally, various additives described above may also be present in a

20   concentrate.

Base Diesel Fuel

The diesel fuels utilized in the preferred embodiments include that portion of crude oil that distills out within the temperature range of approximately 150°C to 370°C (698°F), which is higher than the boiling range of gasoline. Diesel fuel is ignited in an internal combustion engine cylinder

25   by the heat of air under high compression, in contrast to motor gasoline which is ignited by an electrical spark. Because of the mode of ignition, a high cetane number is required in a good diesel fuel. Diesel fuel is close in boiling range and composition to the lighter heating oils. There are two grades of diesel fuel, established by the ASTM: Diesel 1 and Diesel 2. Diesel 1 is a kerosene-type fuel, lighter, more volatile, and cleaner burning than Diesel 2, and is used in engine applications

30   where there are frequent changes in speed and load. Diesel 2 is used in industrial service and No. 4, No. 5 light and heavy, and No. 6 Fuel oil are used in heavy mobile service.

Suitable diesel fuels may include both high and low sulfur fuels. Low sulfur fuels generally include those containing 500 ppm (on a weight basis) or less sulfur, and may contain as little as 100, 95, 90, 85, 80, 75, 70, 65, 60, 55, 50, 45, 40, 35, 30, 25, 20, 15, 20, or 5 ppm or less sulfur, or

35   even 0 ppm sulfur, for example, in the case of synthetic diesel fuels. High sulfur diesel fuels typically include those containing more than 500 ppm sulfur, for example, as much as 1, 2, 3, 4, or 5 wt. % sulfur or more.

Fuels that boil in a range of 150°C to 330°C work best in diesel engines because they are completely consumed during combustion, with no waste of fuel or excess emissions. Paraffins, which offer the best cetane rating, are preferred for diesel blending. The higher the paraffin content of a fuel, the more easily it burns, providing quicker warm-ups and complete combustion. Heavier

5   crude components that boil at higher ranges, although less desirable, may also be used. Naphthenes are the next lightest components and aromatics are the heaviest fractions found in diesel. Using these heavier components helps minimize diesel fuel waxiness. At low temperatures, paraffins tend to solidify, plugging fuel filters.

In addition to Diesel 1 and Diesel 2 fuels, other fuels capable of combusting in a diesel

10   engine may also be used as base fuels in various embodiments. Such fuels may include, but are not limited to, those based on coal dust emulsions and vegetable oil. The vegetable oil based diesel fuels are commercially available and are marketed under the name "bio-diesel." They typically contain a blend of methyl esters of fatty acids of vegetable origin and are often used as an additive to conventional diesel fuels.

15   Cetane Improver

A composition and method for increasing the amount of cetane in fuel is provided. In certain preferred embodiments, the cetane improver comprises beta-carotene or another carotene, carotenoid, derivative or precursor thereof in combination with one or more stabilizing compounds. In other preferred embodiments, the cetane improver comprises encapsulated or otherwise

20   preserved or protected beta-carotene or another carotene, carotenoid, derivative or precursor thereof, optionally in combination with one or more stabilizing compounds.

Beta-Carotene, when encapsulated or in the presence of a stabilizing compound, raises the level of cetane in No. 2 diesel fuel more effectively and maintains the raised cetane level longer than beta-carotene prepared by conventional methods. In preferred embodiments, a cetane

25   improver is prepared by mixing beta-carotene with a stabilizer, such as ethoxyquin, and adding an alkyl nitrate, for example, 2-ethylhexyl nitrate. The preferred cetane improver prepared by the methods described herein increases the level of cetane in No. 2 diesel fuel in a synergistic fashion.

In a preferred embodiment, the cetane improver formulation can be formulated by the following method. Three grams of beta-carotene (1.6 million International units of vitamin A

30   activity per gram) and 3 grams of ethoxyquin are dissolved in 200 ml of a liquid hydrocarbon carrier comprising toluene. It is preferred to dissolve the beta-carotene and ethoxyquin with heating and stirring. Next, approximately 946 milliliters of a 100% solution of 2-ethylhexyl nitrate is added to the mixture and toluene is added so as to obtain a total volume of 3.785 liters. It is not necessary to prepare the cetane improver formulation under inert atmosphere, although it is

35   acceptable to do so. One or more of the fuel additives recited above may also be added to the cetane improver formulation, as desired.

It is to be understood that pure 2-ethylhexyl nitrate is particularly preferred as an optional additive, but that other alkyl nitrates or other grades of 2-ethylhexyl nitrate are also suitable. Further, one of skill in the art will appreciate that other alkyl nitrates or conventional cetane improvers or ignition accelerators, as described above, perform similarly to 2-ethylhexyl nitrate and

5   can be substituted accordingly. Desirably, many different formulations of cetane improver may be made, each having a different alkyl nitrate or more than one alkyl nitrate and/or proportions thereof relative to the beta-carotene. Certain such formulations were evaluated for the ability to raise cetane levels in No. 2 diesel fuel according to the methods described below. In the embodiment described above, it is desirable to add the ingredients in the order described above. However, in

10   other embodiments, variations in the order of addition can be made.

The cetane improver prepared as described above is one embodiment of a "concentrated cetane improver." To improve the cetane level in No. 2 diesel fuel, it is preferred to add from about 0.1 ml or less to about 70 ml or more of the cetane improver described above per one gallon No. 2 diesel fuel. Preferably, the amount of concentrated cetane improver added to a gallon of No. 2

15   diesel fuel is in the range from about 0.3 ml to about 30 ml or 35 ml, more desirably, from about 0.5 ml to about 25 ml, still more preferably, from about 0.75 ml to about 20 ml, even more preferably, from about 1 ml to about 15 ml, and most preferably, from about 2, 3, 4, or 5 ml to about 6, 7, 8, 9, 10, 11, 12, 13, or 14 ml. Similar treat rates may be utilized for other diesel fuels, including high sulfur diesel fuels, low sulfur diesel fuels, poor quality diesel fuels, high quality diesel fuels,

20   biodiesel fuels, and the like.

Although the above additive levels may be preferred for certain embodiments, in other embodiments it may be preferred to have other additive levels. For example, an additive comprising 125 ml of 2-ethylhexyl nitrate to 0.49 g beta-carotene and q.s. toluene to yield 500 ml additive total ("OR-CT") may be present at about 0.05 ml per gallon additized fuel or less up to

25   about 100 ml per gallon additized fuel or more, preferably at about 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8 or 0.9 ml up to about 10, 15, 20, 30, 40 or 50 ml, and most preferably at about 1, 1.5, 2, 2.5, 3, 3.5 or 4 ml up to about 4.5, 5, 6, 7, 8, 9 or 10 ml. To this additized fuel containing the OR-CT additive may be added ethoxyquin at about 0.05 ml per gallon additized fuel or less up to about 100 ml per gallon additized fuel or more, preferably at about 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8 or 0.9 ml up to about 10,

30   15, 20, 30, 40 or 50 ml, and most preferably at about 1, 1.5, 2, 2.5, 3, 3.5 or 4 ml up to about 4.5, 5, 6, 7, 8, 9 or 10 ml.

In other embodiments, preferred fuels contain beta-carotene without any 2-ethylhexyl nitrate added. In those embodiments, an additive comprising 0.49 g beta-carotene and q.s. toluene to yield 500 ml additive may be added to yield a treat rate of from about 0.05 ml per gallon

35   additized fuel or less to about 100 ml (or g) per gallon additized fuel or more, preferably from about 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8 or 0.9 ml (or g) to about 10, 15, 20, 30, 40 or 50 ml (or g), and most preferably from about 1, 1.5, 2, 2.5, 3, 3.5 or 4 ml (or g) up to about 4.5, 5, 6, 7, 8, 9 or 10 ml (or g).

Levels of ethoxyquin or other stabilizer(s) added may range from about 0.05 ml or less per gallon additized fuel or less to about 100 ml or more per gallon additized fuel, preferably from about 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8 or 0.9 ml (or g) to about 10, 15, 20, 30, 40 or 50 ml (or g), and most preferably from about 1, 1.5, 2, 2.5, 3, 3.5 or 4 ml (or g) to about 4.5, 5, 6, 7, 8, 9 or 10 ml (or g).

5   These treat rates are preferred whether the beta-carotene is in pure form or is encapsulated or otherwise preserved or protected.

Appropriate substitutions for beta-carotene and/or ethoxyquin may be made, with an appropriate adjustment in additive levels, if desired. However the above additive levels are generally preferred for substitutions as well. In certain embodiments, higher or lower treat rates

10   may be preferred.

Examples

Fuel additives of certain preferred embodiments may be prepared according to the following descriptions. In other embodiments, other methods of preparing the additives may be preferred. Modifications to these methods, including the order of addition of ingredients,

15   substitutions of ingredients as described above, the use of various diluents, the equipment utilized, mixing conditions, and other aspects of the methods, are all contemplated.

Various cetane improving additive formulations were tested in base diesel fuels. Cetane testing was performed by independent petroleum laboratories, each of which was CARB, EPA, and ASTM Certified. The procedure for testing Cetane is ASTM D-613, a published procedure that

20   measures the ignition point of No. 2 diesel fuel. The test data, provided in Tables 1 and 2, verify that the cetane improver described herein synergistically improves the level of cetane in No. 2 diesel fuel.

Additive OR-CT was prepared which contained 395.8 parts by weight toluene to 660.6 parts by weight of 2-ethylhexyl nitrate to 0.53 parts by weight of beta-carotene. Various samples of

25   No. 2 diesel fuel were treated to contain 1057 ppm of additive OR-CT (referred to as a "2+2" fuel). An additized fuel referred to as "1+0.5" in the following tables corresponds to a fuel treated with 264 ppm OR-CT and 132 ppm 2-ethylhexyl nitrate. Additized fuel referred to as "4+4" contains 1057 ppm OR-CT and 1057 ppm 2-ethylhexyl nitrate, and additized fuel referred to as "8+8" contains 2114 ppm OR-CT and 2114 ppm 2-ethylhexyl nitrate.

30   Table 1 provides baseline cetane number data. Data include cetane numbers for base fuels including various No. 2 diesel fuels, base fuels additized with the conventional cetane improver 2-ethylhexyl nitrate, and base fuels additized with OR-CT prepared under an inert atmosphere.

35

Table 1.

Formulation	Cetane Number	Change over Baseline
Baseline fuel - No. 2 Diesel	44.8	---
No. 2 diesel with 8 ml 100% 2-ethylhexyl nitrate added	51.8	+7
No. 2 diesel "8+8"	54.4	+9.6
Baseline fuel - No. 2 Diesel + 2-ethylhexyl nitrate pretreat	42.5	---
No. 2 diesel + 2-ethylhexyl nitrate pretreat "4+4"	44.6	+2.1
Baseline fuel - No. 2 Diesel	37.0	---
No. 2 diesel with 8 ml 100% 2-ethylhexyl nitrate added	41.8	+4.8
No. 2 diesel "4+4"	41.9	+4.9
No. 2 diesel "8+8"	43.3	+6.3
Baseline fuel - No. 2 Diesel	32.7	---
No. 2 diesel with 8 ml 100% 2-ethylhexyl nitrate added	39.4	+6.7
No. 2 diesel "4+4"	37.3	+4.6
No. 2 diesel "8+8"	41.4	+8.7
Baseline fuel - No. 2 Diesel	40.6	---
No. 2 diesel with 8 ml 100% 2-ethylhexyl nitrate added	46.0	+5.4
No. 2 diesel "2+2"	42.6	+2.0
No. 2 diesel "4+4"	45.6	+5.0
Baseline fuel - No. 2 Diesel	34.9	---
No. 2 diesel with 1.5 ml 100% 2-ethylhexyl nitrate added	39.9	+5.0
No. 2 diesel with "1+0.5"	38.8	+3.9
Baseline fuel - No. 2 Diesel	36.4	---
No. 2 diesel with 4 ml 100% 2-ethylhexyl nitrate added	40.3	+3.9
No. 2 diesel "2+2"	40.7	+4.3
Baseline fuel - No. 2 Diesel	42.2	---
No. 2 diesel "4+4"	50.7	+8.5
No. 2 diesel "8+8"	60.0	+17.3
Baseline fuel - No. 2 Diesel	47.8	---
No. 2 diesel "4+4"	57.4	+9.6
No. 2 diesel "8+8"	62.5	+14.7
Baseline fuel - No. 2 Diesel	51.3	---
No. 2 diesel "4+4"	61.0	+9.7
No. 2 diesel "8+8"	70.5	+19.2
Baseline fuel - No. 2 Diesel	22.9	---
No. 2 diesel "4+4"	31.6	+8.7
No. 2 diesel "8+8"	36.6	+13.7
Baseline fuel - No. 2 Diesel	31.8	---
No. 2 diesel "4+4"	39.1	+7.3
No. 2 diesel "8+8"	42.1	+10.3
Baseline fuel - No. 2 Diesel	38.0	---
No. 2 diesel "4+4"	48.5	+10.5
No. 2 diesel "8+8"	51.1	+13.1
Baseline fuel - No. 2 Diesel	49.2	---
No. 2 diesel "4+4"	54.6	+5.4
No. 2 diesel "8+8"	62.5	+13.3

Diesel fuel formulations containing the cetane improving formulations of preferred embodiments were prepared and cetane numbers compared to control diesel fuels. Air was bubbled through samples designated "w/o nitrogen." Samples designated "w/ nitrogen" were prepared under inert atmosphere. No 2-EHN was separately added to any of the treated samples designated as "4 + 0." Ethoxyquin was added to the formulations designated by "+ ethoxyquin." The base fuel used in the experiments reported in Tables 2 and 3 was a Imperial Oil "clear" diesel fuel basestock. The base fuel used in the experiments reported in Table 4 was a Petro-Canada "clear" diesel fuel basestock.

Table 2.

Sample Number	Cetane Number	Change	Treat Rate
1	37.8	--	base fuel
2	40.9	+ 3.1	2 + 2 (w/ nitrogen)
3	42.5	+ 4.7	4 + 4 (w/ nitrogen)
4	40.5	+ 2.7	2 + 2 (w/o nitrogen) (+ ethoxyquin)
5	42.3	+ 4.5	4 + 4 (w/o nitrogen) (+ ethoxyquin)

Table 3.

Sample Number	Cetane Number	Change	Treat Rate
6	36.8	--	base fuel
7	42.2	+ 5.4	4 + 4 (w/o nitrogen)
8	43.6	+ 6.8	8 + 8 (w/o nitrogen)
9	41.4	+ 4.6	4 + 4 (w/o nitrogen) (+ ethoxyquin)
10	44.9	+ 8.1	8 + 8 (w/o nitrogen) (+ ethoxyquin)

Table 4.

Sample Number	Cetane Number	Change	Treat Rate
11	51.8 (neat)	--	base fuel
12	49.2	- 2.6	4 + 0 (w/o nitrogen)
13	50.1	- 1.7	4 + 0 (w/o nitrogen)
14	54.9	+ 3.1	4 + 0 (w/o nitrogen) (+ ethoxyquin)
15	55.5	+ 3.7	4 + 0 (w/o nitrogen) (+ ethoxyquin)

The comparative data in Tables 2-4 clearly demonstrate the protective effect of ethoxyquin on the cetane improving properties of beta-carotene even under harsh oxidative conditions (namely, bubbling air through the sample for several minutes).

Table 5 provides a description of five diesel fuel samples tested to further quantify the effects of exposure to air of fuels treated with conventional additives and additives of preferred embodiments. Additive OR-CT-A described below contained 125 ml of 2-ethylhexyl nitrate to

0.49 g beta-carotene and q.s. toluene to yield 500 ml additive (prepared under inert atmosphere). The OR-CT-A additive was added to selected samples to yield an effective treat rate as reported in the table. Supplemental 2EHN was added to selected samples. The total sample size for each sample was 950 ml. Samples 4a-5a were subject to an aeration step (shaking under ambient

5   conditions). Samples 3a-5a were stored under an air headspace. Samples 1a-2a were prepared under an inert atmosphere and stored under an inert headspace. The time between preparation of the fuel sample (including aeration, if performed) and octane testing was over three days for each sample.

10   Table 5.

Sample	Ethoxyquin added to sample (ml)	Additive OR-CT (effective treat rate in ml per gallon)	Supplemental 2EHN (treat rate in ml per gallon)	Equivalent OR-CT -A (treat rate in ppm)	Equivalent Supplemental 2EHN (treat rate in ppm)	Air	Inert Atm.	Cetane Number
1a	0	2	2	528.5	528.5	no	yes	40.9
2a	0	4	4	1057	1057	no	yes	42.5
3a	0	0	0	0	0	no	no	37.8
4a	1	2	2	528.5	528.5	yes	no	40.5
5a	1	4	4	1057	1057	yes	no	42.3

The data demonstrate that similar octane improving performance is observed for a beta-carotene containing a formulation prepared under an inert atmosphere with no ethoxyquin added as for a beta-carotene- and ethoxyquin-containing formulation prepared under ambient conditions.

15   The protective effects of ethoxyquin in an aerated diesel fuel containing beta-carotene as a cetane improving additive were determined. Table 6 provides a description of the five diesel fuel samples tested. Additive OR-CT-B contained 250 ml of 2-ethylhexyl nitrate to 1 g beta-carotene to 0.25 g ethoxyquin and q.s. toluene to yield 1000 ml additive. The OR-CT-B additive was added to selected samples to yield an effective treat rate as reported in the table. Supplemental 2EHN was

20   added to selected samples. Ethoxyquin was added to Samples 3b-4b. The total sample size for each sample was 950 ml. Each sample was subjected to an aeration step wherein air at 20 psi was bubbled through the additized sample for 20 minutes. Such aeration conditions are substantially more severe than any ambient atmosphere conditions to which a fuel may be exposed in the field. Cetane test results were as follows.

25

Table 6.

Sample	Ethoxyquin added to sample (ml)	Additive OR-CT-B (effective treat rate in ml per gallon)	Supplemental 2EHN (treat rate in ml per gallon)	Cetane Number
1b	0	4	4	42.2
2b	0	8	8	43.6
3b	1	4	4	41.4
4b	1	8	8	44.9
5b	0	0	0	36.8

   Diesel fuels containing ethoxyquin and beta-carotene as the sole additives were tested for cetane improving properties. Table 7 provides a description of the five diesel fuel samples tested. Samples 3c and 5c were prepared under ambient conditions. Samples 2c and 4c were prepared under inert atmosphere, but the cap to the storage container was left off the samples for 15 minutes to expose the samples to ambient conditions for that time period. Cetane test results were as follows.

Table 7.

Sample	Ethoxyquin (ml per gallon)	Beta-Carotene (ml per gallon)	Inert Atmosphere	Cetane Number
0c	0	0	No	51.8
1c	0	4	Yes	49.2
2c	0	4	No	50.1
3c	1	4	Yes	54.9
4c	1	4	No	55.5

   The data demonstrate that the addition of ethoxyquin may result in an effective doubling in cetane number improvement over that observed for beta-carotene alone. Addition of conventional cetane improving additives at typical treat rates generally yield a cetane number improvement of about 2-3 cetane numbers. The OR-CT additives described above with supplemental 2EHN may yield a cetane number improvement of about 5 or more cetane numbers. Beta-Carotene containing formulations to which ethoxyquin has been added may yield a cetane number improvement of about 8 or more cetane numbers.

Gum Inhibitor for Gasoline, Jet, and Other Fuels

   As gasoline ages in the presence of air, chemical changes may occur because certain fuel components will slowly oxidize. These chemical changes contribute to existent gum and potential gum, as described below. This oxidation process may be slowed by adding inhibitor additives to the fuel. Oxidation stability tests predict the ability of the fuel to resist gum formation when stored, but gasoline does have a finite storage life since gum formation cannot be completely eliminated.

Conventional as well as reformulated and oxygenated gasolines generally have a storage life of about six months, but under harsh storage conditions, the storage life can be considerably shortened. Gasoline manufactured by cracking processes contains unsaturated components which may oxidize during storage and form undesirable oxidation products. Any unstable gasoline

5 undergoes oxidation and polymerization under favorable ambient conditions to form gum, a resinous material. These early stage gums may remain in solution and, due to further chemical changes, may be precipitated. Gum formation is generally believed to be the result of chain reactions of unsaturated paraffins initiated by radicals, such as peroxides, and catalyzed by the presence of metals, particularly copper, which have contaminated the fuel during refining and

10 handling operations.

Since gasoline is generally consumed shortly after a vehicle is fueled, storage life is of little consequence to most consumers. However, gasoline distributors, vendors, or even consumers may wish to store gasoline for extended periods of time, e.g., for longer than six months, or under non-optimal storage conditions. Accordingly, an additive that provides superior resistance to formation

15 of gums which enables stored gasoline to perform satisfactorily when used is desirable.

Existent gum is a sticky, tacky, varnish-like material that is objectionable in fuel systems. When present in excess, gum clogs fuel lines, filter and pump screens, and carburetor jets; causes manifold deposits and sticky intake valves; and reduces the knock value of gasoline. Existent gum is the nonvolatile residue present in a gasoline or jet fuel. Results of existent gum tests indicate the

20 quantity of gum deposit that may occur if the product is used immediately, but not the quantity of gum that may form when the product is stored. ASTM test D381 for Existent Gum in Fuels by Jet Evaporation is used to measure the gum (oxidation products) which are formed before or during the test. In most instances, it can be assumed that the low gum formation will ensure absence of induction-system difficulties. On the other hand, large quantities of gum in aviation turbine fuels is

25 indicative of contamination of fuel by higher boiling oils or particulate matter and generally reflect poor handling practices in distribution downstream of the refinery. High gum can cause deposits and sticking of intake valves in automobile engines.

Potential gum (indicative of oxidation stability) is determined by a test that indicates the presence of gum forming materials and the relative tendency of gasolines and jet fuels to form gums

30 after a specified period of accelerated aging. This value is used as an indication of the tendency of fuels to form gum during extended storage. When added to fuels, inhibitors retard gum formation but will not reduce gum that has already been formed. The effects of potential gum are similar to those described for existent gum. For automotive gasolines, the potential gum may be expressed as the "induction period" (sometimes called the breakdown time). This is a measure of the time (in

35 minutes) elapsed during the accelerated test until the fuel absorbs oxygen rapidly. For aviation gasoline and jet fuel, the potential gum may be expressed as the "potential or accelerated gum." This is the gum plus lead deposits (from leaded fuels) measured at the end of a specified accelerated

aging (oxidation) period. ASTM test D525 for Oxidation Stability of Gasoline (Induction Period Method) utilizes accelerated oxidation conditions to determine the stability of finished gasolines. The induction period may be used as an indication of the tendency of motor gasoline to form gum in storage, i.e., potential gum.

5   Quinolines, including dihydroquinolines such as ethoxyquin, are particularly preferred for use in fuels to inhibit gum formation, especially gum as measured by potential or accelerated gum tests. The quinoline may be added to the fuel at levels typical of other gum inhibitors. Depending upon the severity of the fuel, the quinoline may be added at a level of less than 1 ppm or at a level of 2, 3, 4, 5, 6, 7, 8, 9, or 10 ppm or more, preferably 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65,
10   70, 75, 80, 85, 90, 95, or 100 ppm or more, more preferably about 100, 150, 200, 250, 300, 350, 400, 450, or 500 ppm or more. If the fuel is particularly severe, i.e., the base fuel has a high potential gum, then it may be desirable to add the quinoline at a level of 600, 650, 700, 750, 800, 850, 900, 950, 1000, 2000, 3000, or 4000 ppm or more. In a particularly preferred embodiment, ethoxyquin is added to gasoline at a level of 50 to 750 ppm, preferably, 100 to 500 ppm, and more
15   preferably 200 or 400 ppm.

The gasolines utilized in the practice of various embodiments can be traditional blends or mixtures of hydrocarbons in the gasoline boiling range, or they can contain oxygenated blending components such as alcohols and/or ethers having suitable boiling temperatures and appropriate fuel solubility, such as methanol, ethanol, methyl tert-butyl ether (MTBE), ethyl tert-butyl ether
20   (ETBE), tert-amyl methyl ether (TAME), and mixed oxygen-containing products formed by "oxygenating" gasolines and/or olefinic hydrocarbons falling in the gasoline boiling range. Thus various embodiments involve the use of gasolines, including the so-called reformulated gasolines which are designed to satisfy various governmental regulations concerning composition of the base fuel itself, components used in the fuel, performance criteria, toxicological considerations and/or
25   environmental considerations. The amounts of oxygenated components, detergents, antioxidants, demulsifiers, and the like that are used in the fuels can thus be varied to satisfy any applicable government regulations.

Aviation gasoline is especially for aviation piston engines, with an octane number suited to the engine, a freezing point of -60°C, and a distillation range usually within the limits of 30°C and
30   180°C.

Gasolines suitable for used in preferred embodiments also include those used to fuel two-cycle (2T) engines. In two-cycle engines, lubrication oil is added to the combustion chamber and admixed with gasoline. Combustion results in emissions of unburned fuel and black smoke. Certain two-cycle engines may be so inefficient that 2 hours of running such an engine under load
35   may produce the same amount of pollution as a gasoline-powered car equipped with a typical emission control system that is driven 130,000 miles. In a typical two-cycle engine vehicle, 25 to

30% of the fuel leaves the tailpipe unburned. In California alone there are approximately 500,000 two-cycle engines, which produce the equivalent of the emissions of 4,000,000 million gasoline powered cars. In Malaysia and throughout much of Asia, China and India the problem is much more severe. Malaysia has 4,000,000 two-cycle engines, which produce pollution equivalent to that

5   from 32,000,000 automobiles.

Quinolines such as ethoxyquin may be added to any liquid hydrocarbonaceous fuel succeptible to gum formation, including diesel fuels, jet fuels, and resid fuels. Treat rates may be similar to those used for gasoline, however it may be preferred to adjust the treat rate up or down depending upon the severity of the fuels and its susceptibility to gum formation.

10   The above description discloses several methods and materials of the present invention. This invention is susceptible to modifications in the methods and materials, such as the choice of base fuel, the components selected for the base formulation, as well as alterations in the formulation of fuels and additive mixtures. Such modifications will become apparent to those skilled in the art from a consideration of this disclosure or practice of the invention disclosed herein. Consequently,

15   it is not intended that this invention be limited to the specific embodiments disclosed herein, but that it cover all modifications and alternatives coming within the true scope and spirit of the invention as embodied in the attached claims.